



CATALYTIC FLASH PYROLYSIS OF  
BIOMASS:

CATALYST AND PROCESS  
DEVELOPMENT FOR PRODUCTION  
OF A FUEL PRECURSOR

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CATALYTIC FLASH PYROLYSIS OF BIOMASS:  
CATALYST AND PROCESS DEVELOPMENT  
FOR PRODUCTION OF A FUEL PRECURSOR

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Dedicated to Abu Jee, Ami Jee, Bhai Jan, and Baji Jan

ابو جی امی جی بھائی جان اور باجی جان کے نام  
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## Summary

Flash pyrolysis of biomass is a promising technology to produce pyrolysis-oil (bio-oil). However, the presently produced bio-oil is not suitable for direct use as a transportation fuel or as a fuel additive/precursor. The presence of oxygenated compounds in the bio-oil mainly contributes to its deleterious properties such as high viscosity, high acidity and resulting corrosiveness, instability upon storage, lower energy density than the conventional fuels by 50%, incompatibility and immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure of air. Catalytic de-oxygenation is considered as a first line option to overcome the problematic characteristics of the bio-oil. However, the challenge in de-oxygenation catalyst development is to design a catalyst that selectively removes the problematic oxygenates in the bio-oil and not the desired components. This thesis aims to develop an efficient in-situ de-oxygenation catalyst to upgrade bio-oil into a high-quality fuel precursor. The second part of the thesis is focused on the catalytic flash pyrolysis of different triglycerides containing lignocellulosic feedstocks and triglycerides incorporated wood. The here applied online catalytic flash pyrolysis aims at the production of a hydrocarbons rich bio-oil that can be readily refined into transportation fuels using conventional technologies.

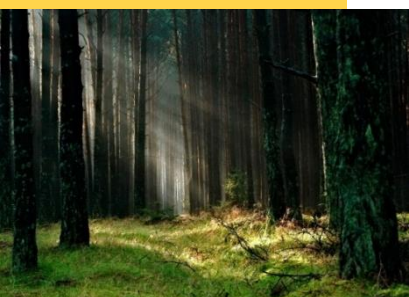
Chapter 2 describes a literature review on catalyst systems and online catalytic upgrading of bio-oil for fuel application. Extensive research has been reported on online catalytic upgrading of bio-oil and Chapter 2 gives an overview of the progresses and state-of-art in this field of research. In this review chapter, the performance of different catalysts used for online catalytic upgrading of bio-oil has been systematically reviewed with respect to the scale of application e.g. analytical, bench and pilot scale. The scale of application is an important aspect to be covered because many catalysts could not perform well after up-scaling from an analytical to a bench scale system. To review the performance of catalyst systems, catalysts have been categorized in different families and a systematic evaluation of the catalyst effect on pyrolysis products and product characteristics has been carried out with respect to the scale of experimental setup. Microporous zeolites are ranked at the top in performance to tailor the desired bio-oil properties. Main credits to the zeolites are deoxygenation and decreased molecular weight of the bio-oil, and main drawbacks are a decrease in the yield of the organic phase of the bio-oil and catalyst deactivation by coke deposition. Mesoporous aluminosilicates are not performing better than zeolites and show a relatively lower activity compared to zeolites. Research on alkaline compounds for catalytic pyrolysis of biomass is not extensive. Preliminary results show their potential for de-oxygenation of bio-oil, for production of hydrocarbons, and for the reduction of undesired compounds that need to be further investigated systematically.

Chapter 3 is aimed to study the alkali-cation modified zeolites at a lab scale unit and to use online pyrolysis vapor fractionation to further improve the quality of catalytic bio-oil. Many researchers claimed potential of zeolites for in-situ upgrading of bio-oil at analytical scale testing but zeolites failed to perform well at bench/lab scale pyrolysis units as discussed in Chapter 2. Modified zeolites are investigated to study the effect of varying acidities of Faujasite Y zeolites, zeolite structures (ZSM5), different catalyst to biomass ratios and different catalytic pyrolysis temperatures at a lab scale unit of 1 kg/h feedstock

capacity. High catalyst/biomass ratios showed some deoxygenation of the bio-oil. Modified zeolites decreased the organic liquid yield due to the increase of the production of non-condensables, primarily hydrocarbons, and the produced bio-oil was less viscous. Zeolites were effective to crack heavy molecular weight compounds in the bio-oil. Acidic zeolites such as H-Y and H-ZSM5, increased the desirable chemical compounds in the bio-oil such as phenols, furans and hydrocarbon, and reduced the undesired compounds such as acids. On the other hand reducing the acidity of zeolites reduced some of the undesired compounds in the bio-oil such as ketones and aldehydes. The H-Y performance was superior to the rest of zeolites studied: bio-oil of better chemical and calorific value was produced with a high organic liquid yield and low oxygen content. H-ZSM5 was a close competitor to H-Y in performance but with a lower yield of bio-oil. However, overall performance of modified zeolites is not up to the mark to tailor the desired bio-oil properties and they cannot be the first choice catalyst for in-situ upgrading of bio-oil. In the second part of Chapter 3, an integrated approach is studied to improve the quality of catalytic bio-oil where in-situ catalysis and fractionation of pyrolysis vapors is combined in a single process. A high calorific value bio-oil with 90% organics, has been produced using integrated flash pyrolysis, in-situ catalysis and fractionation of pyrolysis via two stage condensation.

Although the zeolites performed some de-oxygenation, the downside is the occurrence of unwanted cracking and a low yield; the thus produced bio-oil is far from the desired properties of a fuel precursor.

In Chapter 4, a novel alumina-supported sodium carbonate catalyst ( $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ) has been developed and investigated. The effect of catalyst on the quality of the bio-oil has been presented for two different reactor systems. The  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalyst has been developed based on systematic studies at analytical scale with batch experiments using 2 gram of biomass and a fixed bed catalyst reactor. As mentioned earlier, often the catalyst system tested at analytical scale failed to perform well at larger scale experimental setups. In the present work,  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  has been investigated in a bench scale unit of 1 kg/h biomass capacity that consists of an entrained flow pyrolysis reactor. Ex-situ catalytic pyrolysis (post treatment of the pyrolysis vapor) was carried out in a downstream catalytic fixed bed reactor to study the effect of the catalytic reaction temperature and to exclude problems such as bad catalyst/vapor contact that may occur for in-situ applications of catalysts. As the downstream fixed bed reactor system is not feasible to scale up for commercial applications as continuous regeneration is required, in-situ upgrading of pyrolysis vapor was carried out in an entrained flow reactor system with a premixed feedstock of catalyst and biomass to simulate the condition of a commercial system such as in e.g. a fluidized bed reactor.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  seemed to be very effective for the de-oxygenation of the pyrolysis liquid and the oxygen content of the bio-oil was decreased from 47.5 wt.% to 16.4 wt.%. An organic rich bio-oil was obtained with only 5.8 wt.% water content and a higher heating value of 36.1 MJ/kg. Carboxylic acids were completely removed and the bio-oil had almost a neutral pH. In-situ catalytic upgrading of biomass pyrolysis vapors showed a very similar bio-oil quality compared to the post-treatment of pyrolysis vapors over the catalytic fixed bed. This results supports the possible application of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  in a commercial type reactor system such as a fluidized bed reactor or vortex reactor. High-quality bio-oil produced with  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  in both catalyst reactor systems, have a high significance towards the production of a green fuel precursor.



The focus in Chapter 5 is on the production of hydrocarbon-rich bio-oil. In the previous chapter, the catalytic pyrolysis process of wood produced a highly deoxygenated bio-oil at lab scale studies but the produced oil had a low content in hydrocarbons, and was enriched with ketones and phenols compounds. In Chapter 5, triglycerides contained biomass feedstocks are studied for catalytic pyrolysis. A vegetable-oil-impregnated wood is used as a model case and a triglycerides inherited jatropha cake is used for practical case. The aim is to produce a hydrocarbon rich bio-oil with triglycerides contained biomass. Catalytic pyrolysis of both types of biomass, vegetable-oil-impregnated wood and jatropha cake, are compared using sodium based catalysts (sodium carbonate and  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ). The catalytic pyrolysis is carried out in two modes: in-situ catalytic pyrolysis and ex-situ catalytic pyrolysis. The in-situ catalytic pyrolysis is carried out in an entrained flow reactor system using a premixed feedstock of  $\text{Na}_2\text{CO}_3$  and biomass, and post-treatment of the biomass pyrolysis vapor is conducted in a downstream fixed bed reactor of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ . The results show that both  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  can be used for the production of a high-quality hydrocarbons-rich bio-oil from catalytic pyrolysis of oil-impregnated wood and jatropha cake. The catalytic bio-oil has a very low oxygen content, a low water content of 1 wt-%, a neutral pH, and a high-calorific value up to 41.8 MJ/kg. The bio-oil consisted of high-value chemical compounds, mainly hydrocarbons, while the undesired compounds in the bio-oil are either completely removed or considerably reduced. Increasing the triglycerides content (vegetable oil) in the wood enhanced the formation of hydrocarbons in the bio-oil. Post-treatment of the pyrolysis vapor over a fixed bed of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  produced superior quality bio-oil compared to in-situ catalytic pyrolysis with  $\text{Na}_2\text{CO}_3$ . The reason could be the good performance of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  and the good catalyst/vapor contact in a catalytic fixed bed reactor. This high-quality and hydrocarbons-rich bio-oil looks very promising as a precursor for the production of alternative transportation fuels.

Chapter 6, the effect of a  $\text{Na}_2\text{CO}_3$  catalyst system on the primary reaction kinetics of biomass pyrolysis has been investigated in a novel thermogravimetric vortex reactor system. About 40 wt.% of  $\text{Na}_2\text{CO}_3$  was impregnated onto the wood using both wet and dry impregnation methods. The effect of the catalyst, the temperature and impregnation methods have been studied. The temperature and catalyst significantly increased the primary reaction kinetics of the wood and decreased the activation energy and thus making the thermal degradation of wood pyrolysis faster. The effect of the catalyst on the primary reaction rates was enhanced with increasing pyrolysis temperature. The wet impregnation of  $\text{Na}_2\text{CO}_3$  was more effective to improve the primary reaction kinetics of biomass pyrolysis compared to the dry impregnation. These findings are important for the application of sodium based catalyst in a pilot scale setup e.g. PyRos which is a vortex reactor system. The main findings have been reported in Chapter 7, with recommendations for further work and an outlook for the future.

# SAMENVATTING

Flash pyrolyse van biomassa is een veelbelovende technologie voor de productie van pyrolyse-olie (bio-olie). De momenteel geproduceerde bio-olie is echter niet geschikt voor rechtstreeks gebruik als een transportbrandstof of als een co-feed voor een raffinaderij. De aanwezigheid van zuurstofverbindingen in de bio-olie draagt vooral bij aan de mindere eigenschappen, zoals hoge viscositeit, hoge zuurgraad en de resulterende corrosiviteit van de brandstof, instabiliteit bij opslag, een lagere energie dichtheid vergeleken met conventionele brandstoffen met 50%, onverenigbaarheid en niet mengbaar met fossiele brandstoffen, thermische instabiliteit en neiging tot polymeriseren onder invloed van lucht. Katalytische de-oxygenatie wordt beschouwd als een goede optie om de problematische kenmerken van de bio-olie verbeteren. Echter de uitdaging in de ontwikkeling van de de-oxygenatie katalysator is dat de katalysator selectief de problematische oxides in de bio-olie verwijderd en niet de gewenste componenten. In dit proefschrift wordt de ontwikkeling van een efficiënte in-situ de-oxygenatie katalysator beschreven voor het upgraden van de bio-olie als voeding bij de productie van een hoge kwaliteit brandstof. Het tweede deel van het proefschrift is gericht op de katalytische flash pyrolyse van verschillende triglyceriden bevattende lignocellulose grondstoffen en hout met opgenomen triglyceriden. De hier toegepaste in-situ katalytische flash pyrolyse proces heeft tot doel: de productie van een koolwaterstoffen rijke bio-olie die gemakkelijk kan worden omgezet naar transport brandstoffen met behulp van conventionele raffinage technologieën.

Hoofdstuk 2 beschrijft een overzicht van de literatuur naar katalytische processen en het in-situ katalytische upgraden van bio-olie voor brandstof toepassingen. Uitgebreid onderzoek is gerapporteerd naar in-situ katalytische verbetering van bio-olie en hoofdstuk 2 geeft een overzicht van de vorderingen en de state-of-art van het onderzoek op dit gebied. In het review hoofdstuk, zijn de prestaties van verschillende katalysatoren voor het gebruikt voor in-situ katalytische upgraden van bio-olie systematisch onderzocht met betrekking tot de omvang van toepassing bijvoorbeeld op analytische schaal, de laboratorium schaal en op pilot plant schaal. De grootte van toepassing is een belangrijk aspect dat aan bod moeten komen omdat veel katalysatoren niet goed presteren na het opschalen van analytische naar een systeem op laboratorium schaal. Om de prestaties van katalytische systemen te beoordelen, zijn de katalysatoren zijn gecategoriseerd in verschillende klassen en een systematische evaluatie van het effect van de katalysator op pyrolyse producten en de product eigenschappen zijn verricht met betrekking tot de grootte van de experimentele opstelling. Microporeuze zeolieten zijn gerangschikt in de top wat betreft de prestaties om de gewenste bio-olie componenten te produceren. Belangrijkste voordelen van de zeolieten zijn de-oxygenering en het lagere molecuulgewicht van de bio-olie. De belangrijkste nadelen zijn een afname van de opbrengst van de organische fractie van de bio-olie en katalysator de-activering door afzetting van de cokes. Mesoporous aluminosilicaten presteren niet beter dan de zeolieten en tonen een relatief lagere activiteit t.o.v. zeolieten. Onderzoek op alkalische verbindingen voor katalytische pyrolyse van biomassa is niet erg uitgebreid. Voorlopige resultaten tonen hun potentieel voor de de-oxygenatie van bio-olie, voor de productie van koolwaterstoffen, en voor het terugdringen van ongewenste verbindingen, deze moet verder systematisch onderzocht worden.



Hoofdstuk 3 beoogt het bestuderen van alkali-cation gemodificeerde zeolieten op een lab schaal eenheid en het aansluitend fractioneren van pyrolyse dampen om de kwaliteit van katalytische bio-olie verder te verbeteren. Meerdere onderzoekers claimen de potentie van zeolieten voor in situ verbeteren van bio-olie op analytische schaal maar de zeolieten presteren niet goed op laboratorium schaal, zoals besproken in hoofdstuk 2. Gemodificeerde zeolieten worden onderzocht om het effect van verschillende te bestuderen zeolieten daalde de opbrengst aan organische vloeistof als gevolg van de toename van de productie van niet-condenseerbare, voornamelijk koolwaterstoffen, en de geproduceerde bio-olie was minder viskeus. Zeolieten waren effectief in het kraken verbindingen met een hoog molecuulgewicht in de bio-olie. Bij het gebruik van zure zeolieten zoals H-Y en H-ZSM5, steeg de opbrengst van de gewenste chemische verbindingen in de bio-olie zoals fenolen, furanen en koolwaterstoffen en verminderd de opbrengst aan ongewenste stoffen zoals zuren. Aan de andere kant het verlagen van de zuurgraad van zeolieten verminderd een aantal de ongewenste verbindingen in de bio-olie zoals ketonen en aldehyden. De prestaties van de H-Y was superieur aan de rest van de bestudeerde zeolieten: bio-olie met een betere chemische en calorische waarde werden geproduceerd en tevens een hoge opbrengst aan vloeibare organisch product en een laag zuurstofgehalte. H-ZSM5 was een nauwe concurrent van H-Y in de prestaties maar met een lagere opbrengst aan bio-olie. De algehele prestatie van gemodificeerde zeolieten is echter niet toereikend om de gewenste bio-olie-eigenschappen aan te passen en zullen niet de eerste keuze-katalysator zijn voor het in-situ verbeteren van bio-olie.

In het tweede deel van hoofdstuk 3, wordt een geïntegreerde aanpak ter verbetering van de kwaliteit van katalytische bio-olie bestudeerd, hier wordt katalyse en fractionering van pyrolyse dampen gecombineerd in één proces. Een hoog calorische bio-olie met 90% organische stoffen, is vervaardigd met behulp van geïntegreerde flash pyrolyse, in-situ katalyse en fractionering van de pyrolyse damp via een tweetraps condensatie.

Hoewel de zeolieten enige de-oxygenatie te zien gaven, is het nadeel ongewenst kraken en een lage opbrengst aan olie; de hier geproduceerde bio-olie is ver van de gewenste samenstelling en nog ver verwijderd van co-feed voor brandstof productie.

In Hoofdstuk 4 is een nieuwe natriumcarbonaat katalysator op basis van aluminiumoxide ( $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$ ) ontwikkeld en onderzocht. Het effect van katalysator op de kwaliteit van de bio-olie is gepresenteerd voor twee verschillende reactorsystemen. De  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$ -katalysator is ontwikkeld op basis van systematische studies op analytische schaal met batch-experimenten met 2 gram biomassa en een katalysatorreactor met vast bed. Zoals eerder vermeld, presteren katalysatorsystemen welke op analytische schaal werden getest vaak niet goed werken grotere schaal. In dit onderzoek is  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  onderzocht in een bench-scale-eenheid met een voeding van 1 kg/uur aan biomassa een pyrolyse reactor. Ex-situ katalytische pyrolyse (nabehandeling van de pyrolysedamp) werd uitgevoerd in een na geschakelde katalytische reactor met een vast bed om het effect van de temperatuur van de katalytische reactie te bestuderen en problemen uit te sluiten zoals een slecht contact tussen katalysator / damp wat kan optreden bij de in-situ toepassingen van katalysatoren. Na geschakelde vast bed reactorsysteem zijn moeilijk zijn op te schalen voor commerciële toepassingen, er is continue regeneratie vereist, hier is de in-situ upgrading van de pyrolyse dampen uitgevoerd in een meestroom reactorsysteem (entrained flow) met een vooraf gemengde

voeding van katalysator en biomassa om de toestand te simuleren van een commercieel systeem zoals in bijvoorbeeld een wervelbedreactor.  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  leek zeer effectief te zijn voor de de-oxygenering van de pyrolyse dampen, het zuurstofgehalte van de bio-olie was afgenomen van 47,5 gewichtsprocent tot 16,4 gewichtsprocent. Een organisch rijke bio-olie werd verkregen met slechts 5,8 gew.% water en een hogere calorische van 36,1 MJ / kg. Carbonzuren werden volledig verwijderd en de bio-olie had bijna een neutrale pH. In-situ katalytische opwaardering van de pyrolyse dampen van biomassa vertoonde een zeer vergelijkbare bio-olie kwaliteit t.o.v. de nabehandeling van pyrolyse dampen over een katalytisch vast bed. Deze resultaten ondersteunen de mogelijke toepassing van  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  in een commercieel reactorsysteem zoals een gefluidiseerd bed reactor of een vortexreactor. Hoogwaardige bio-olie geproduceerd met  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  in beide katalysatorreactorsystemen, heeft een grote waarde voor de eventuele productie van een groene feed in de brandstofproductie.

De focus in hoofdstuk 5 ligt op de productie van een koolwaterstofrijke bio-olie. In het vorige hoofdstuk, produceerde het katalytische pyrolyseproces van hout een sterk gedeoxygeneerde bio-olie op laboratoriumschaal, maar de geproduceerde olie had een laag gehalte aan koolwaterstoffen en was verrijkt met ketonen en fenolen. In Hoofdstuk 5 worden triglyceriden bevattende biomassa stromen bestudeerd voor katalytische pyrolyse. Een met plantaardige olie geïmpregneerd hout wordt als een modelstof gebruikt en een met triglyceriden bevattende jatropha-cake wordt in de praktijk gebruikt. Het doel is om een koolwaterstofrijke bio-olie te produceren met biomassa die triglyceriden bevat. Katalytische pyrolyse van beide soorten biomassa, met plantaardige olie geïmpregneerd hout en jatropha-cake, worden vergeleken met gebruik maken van op natrium gebaseerde katalysatoren (natriumcarbonaat en  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$ ). De katalytische pyrolyse wordt op twee manieren uitgevoerd: in-situ katalytische pyrolyse en ex-situ katalytische pyrolyse. De in situ katalytische pyrolyse wordt uitgevoerd in een entrained flow reactor met een vooraf gemengd voedingsmateriaal van  $\text{Na}_2\text{CO}_3$  en biomassa, en nabehandeling van de biomassa pyrolyse-damp wordt uitgevoerd in een na geschakelde vast bed reactor van  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$ . De resultaten laten zien dat zowel  $\text{Na}_2\text{CO}_3$  als  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  kunnen worden gebruikt voor de productie van een hoogwaardige koolwaterstofrijke bio-olie met katalytische pyrolyse van met olie geïmpregneerd hout of jatropha-cake. De katalytische bio-olie heeft een zeer laag zuurstofgehalte, een laag watergehalte van 1 gew.%, een neutrale pH en een hoge calorische waarde tot 41,8 MJ / kg. De bio-olie bestaat uit hoogwaardige chemische verbindingen, voornamelijk koolwaterstoffen, terwijl de ongewenste verbindingen in de bio-olie volledig worden verwijderd of aanzienlijk worden verminderd. Toename van het triglyceridengehalte (plantaardige olie) in het hout versterkte de vorming van koolwaterstoffen in de bio-olie. Nabehandeling van de pyrolyse-damp over een vast bed van  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  produceerde bio-olie van superieure kwaliteit in vergelijking met in-situ katalytische pyrolyse met  $\text{Na}_2\text{CO}_3$ . De reden zou kunnen zijn van de goede prestaties van  $\text{Na}_2\text{CO}_3$  /  $\gamma\text{-Al}_2\text{O}_3$  en het goede katalysator / dampcontact in een reactor met een katalytisch vast bed. Deze hoogwaardige en koolwaterstofrijke bio-olie ziet er veelbelovend uit als een voeding voor de productie van alternatieve transportbrandstoffen.

Hoofdstuk 6, het effect van een  $\text{Na}_2\text{CO}_3$ -katalysator de primaire reactiekinetiek van biomassapyrolyse is onderzocht in een nieuw ontwikkelde thermogravimetrisch vortexreactor. Ongeveer 40 gew.%  $\text{Na}_2\text{CO}_3$  werd geïmpregneerd op het hout met behulp

van zowel natte als droge impregneermethoden. Het effect van de katalysator, de temperatuur en impregnatiemethoden zijn bestudeerd. De temperatuur en katalysator verhoogden significant de primaire reactiekinetiek van het hout en verminderden de activeringsenergie en maakten aldus de thermische afbraak van houtpyrolyse sneller. Het effect van de katalysator op de primaire reactiesnelheden werd verhoogd met toenemende pyrolysetemperatuur. De natte impregnatie van  $\text{Na}_2\text{CO}_3$  was effectiever om de primaire reactiekinetiek van biomassapyrolyse te verbeteren in vergelijking met de droge impregnatie. Deze bevindingen zijn belangrijk voor de toepassing van op natrium gebaseerde katalysator in een pilot plant, b.v. PyRos, een vortex-reactorsysteem. De belangrijkste bevindingen zijn gerapporteerd in hoofdstuk 7, met aanbevelingen voor verder werk en een vooruitblik op de toekomst.





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# CHAPTER 1:

## Introduction

### 1.1 Preface

Pyrolysis oil (hereinafter "bio-oil") can be produced by flash-pyrolysis of biomass. Flash pyrolysis is a medium temperature (ca. 500°C) thermochemical process in which biomass is rapidly converted to vapors, non-condensable gases and bio-char in the absence of oxygen. After rapid cooling and condensation, a liquid is formed (bio-oil) from the vapors. Reported liquid yields can be as high as 70-75 wt.% (incl. water) for woody biomass types. The bio-oil has advantage over parent biomass including its higher energy density, good storage and transportation properties, and a relatively clean and homogeneous feedstock. Bio-oil has been used successfully as gasifier feedstock, for use in diesel engines, gas turbines and co-feeding in boilers [1-3]. Extensive review on the research, technology, and application of biomass fast pyrolysis has been published [4-7] .

However, bio-oil is also characterized as acidic, corrosive, thermally unstable, polar and highly oxygenated [8-11]. The bio-oil produced with current technologies is not suitable for direct use as a transportation fuel or as a fuel additive [5]; it has a low heating value which is approximately 40-50 wt.% lower than that of fuel oil, it has a high viscosity, a substantial solids content, and it typically contains 25-30 wt.% water that cannot be readily separated making the bio-oil immiscible with conventional fuels [8]. The oxygen content of bio-oil ranges from 30-55 wt % depending upon the originating biomass source [4]. The oxygenated compounds in the bio-oil, derived from cellulose, hemicellulose and lignin, are considered as the main contributor for most of its deleterious properties.

Typical properties of wood pyrolysis bio-oil and heavy fuel oil are compared in **Table 1** [12]. High acidity is a major problematic property of the bio-oil in general and for fuel applications in particular as it leads to the corrosion of material. Besides water, acetic acid is the main organic acid present in the bio-oil with a large quantity of ~5 wt % followed by formic acids (at ~3 wt %) [13]. The acidic and carbonyl compounds present in the bio-oil are responsible for its low pH value and low calorific value. Another crucial problematic property of the bio-oil is the thermal or storage stability that increases the viscosity and/or molecular weight of bio-oil over time. Viscosity is important especially for applications where pumping and injecting of bio-oil are involved. Carbonyl compounds such as aldehydes and ketones are considered to be responsible for the ageing reactions, these reactive oxygenates tend to oligomerize over time leading to chemical instability of bio-oil. Viscosity of bio-oil is correlated with its molecular weight, and large concentrations of heavy components (molecular weight > 1000 g/mol) are responsible for the high

viscosity of bio-oil and may cause problems in the application at the downstream conversion units [14, 15]. Most of the heavy components are lignin derives [16] and the viscosity and stability of bio-oil can be improved by cracking these large molecules into useful lower molecular weight compounds.

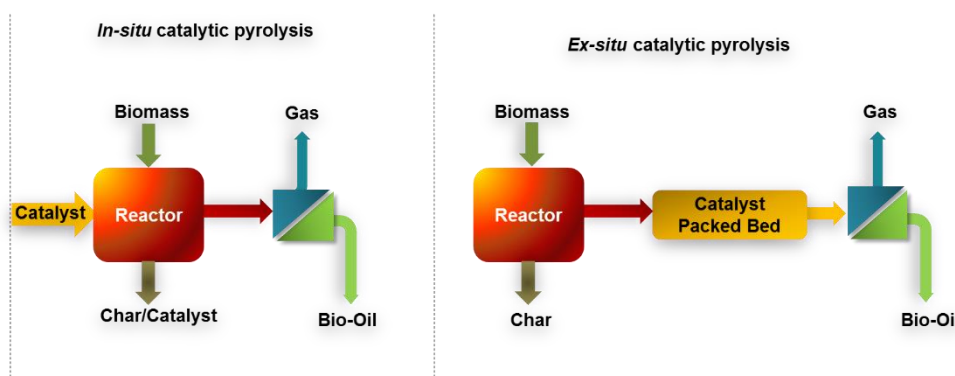
**Table 1:** Typical properties of wood pyrolysis bio-oil and heavy fuel oil [12]

Physical property	Bio-oil	Heavy fuel oil
Moisture content wt. %	15-30%	0.1
pH	2.5	-
Specific gravity	1.2	0.94
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity (at 50°C), cP	40-100	180
Solids, wt. %	0.2-1	1
Distillation residue, wt. %	up to 50	1

Therefore, to improve the quality of the bio-oil, the oxygenated compounds and the lignin derived large molecules need to be removed or reformed into more useful components. There are several options of upgrading and improving the bio-oil quality. One method is the conversion of biomass into bio-oil and then downstream upgrading the bio-oil over a catalyst, for example via hydrodeoxygenation (HDO) and zeolite cracking. Post pyrolysis catalytic upgrading of bio-oil has been extensively reviewed [17-19]. However, research on the catalytic after-treatment of bio-oil has not shown any promising results. Catalytic after-treatment process suffers from fast deactivation of the catalyst caused by coking and poor yield of hydrocarbons due to bypassing of the larger molecules of the bio-oils [15]. HDO appears to have the better potential compared to zeolite cracking, but several issues still have to be addressed before commercialisation of the process, e.g. catalyst development, and sustainable sources for hydrogen.

Online catalytic pyrolysis is considered as one of the options to overcome the problem characteristics of bio-oil. Online catalytic pyrolysis involves the online treatment of pyrolysis vapors before the condensation step. The catalyst is employed either in-situ or ex-situ, the two process schemes are presented in **Figure 1**. Beside deoxygenation of

pyrolysis vapors, in-situ catalytic pyrolysis could also play a role in the primary decomposition of biomass and in promoting reactions of the product gases and vapors. The catalyst for online catalytic pyrolysis is expected to induce the cracking reactions to breakdown the heavy molecules in pyrolysis products to produce lighter and less viscous bio-oil. Catalysts are expected to enhance the reactions that involve the removal of the reactive oxygenated compounds of the bio-oil, especially acidic and carbonyl compounds, and produce a bio-oil with a low oxygen content, a higher heating value and a better stability. Many researchers have shown the positive effects of online catalytic pyrolysis on the quality of the bio-oil and research has been focused to design dedicated catalysts that can increase the formation of high value desired compounds such as hydrocarbon and phenols and can reduce the production of undesirable compounds such as acids and carbonyls.



**Figure 1:** Two process schemes for online catalytic pyrolysis reaction pathway for conversion of bio-oil over zeolite catalysts

Online catalytic treatment of bio-oil vapors is carried out either in the pyrolysis reactor (in-situ) e.g. in a fluidized bed reactor or downstream of the pyrolysis reactor in a separate reactor (ex-situ) e.g. in a packed bed reactor system. Both options can be integrated in existing pyrolysis reactor systems, however, the first option (online) requires less capital investment and offers technical benefits. In the present study the performance of catalysts used for online catalytic pyrolysis in different mode of application, in-situ and ex-situ, have been investigated making use of different experimental setups such as: analytical scale, bench scale and pilot scale.

## 1.2 Catalyst selection criteria for catalytic pyrolysis of biomass

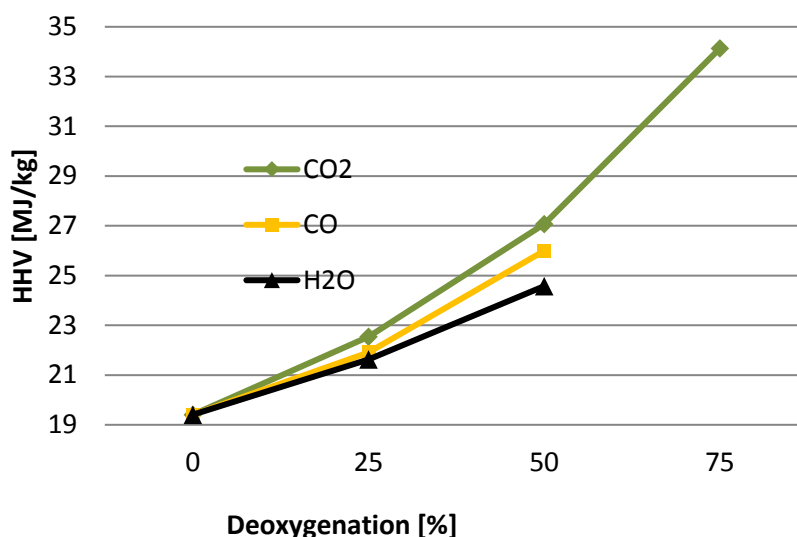
A wide range of organic compounds is found in bio-oil produced via flash pyrolysis of biomass. The identified compounds of organic phase are typically grouped as hydrocarbons, phenols, furans, acids, alcohols, aldehydes, esters, ketones, aromatics, polycyclic aromatic hydrocarbons (PAHs), and heavy compounds. In **Table 2**, the chemical composition of pyrolysis oil derived from maple wood have been described and compounds have been classified according to their chemical nature and identified as desired, undesired and valuable compounds [20]. Hydrocarbons are desirable fractions for fuel application, and compounds like phenol and its alkylated derivatives have high

commercial value especially for the resin or adhesive industry and make the process economically attractive. On the other hand oxygen-containing compounds, such as acids and carbonyls as well as heavy compounds, are considered as undesirable fractions. The reduction of acids is important for the corrosiveness of bio-oil, and the reduction of carbonyls and heavy compounds is important for the stability and storage properties. Reduction of PAH's is important as they are considered as hazardous for the environment. Furans are considered valuable because of their fuel compatibility and high energy value. To improve the quality of bio-oil to be used as a transportation fuel, the promising catalysts would produce more desirable and less undesirable fractions.

**Table 2:** Composition of maple wood derived pyrolysis oil [20]

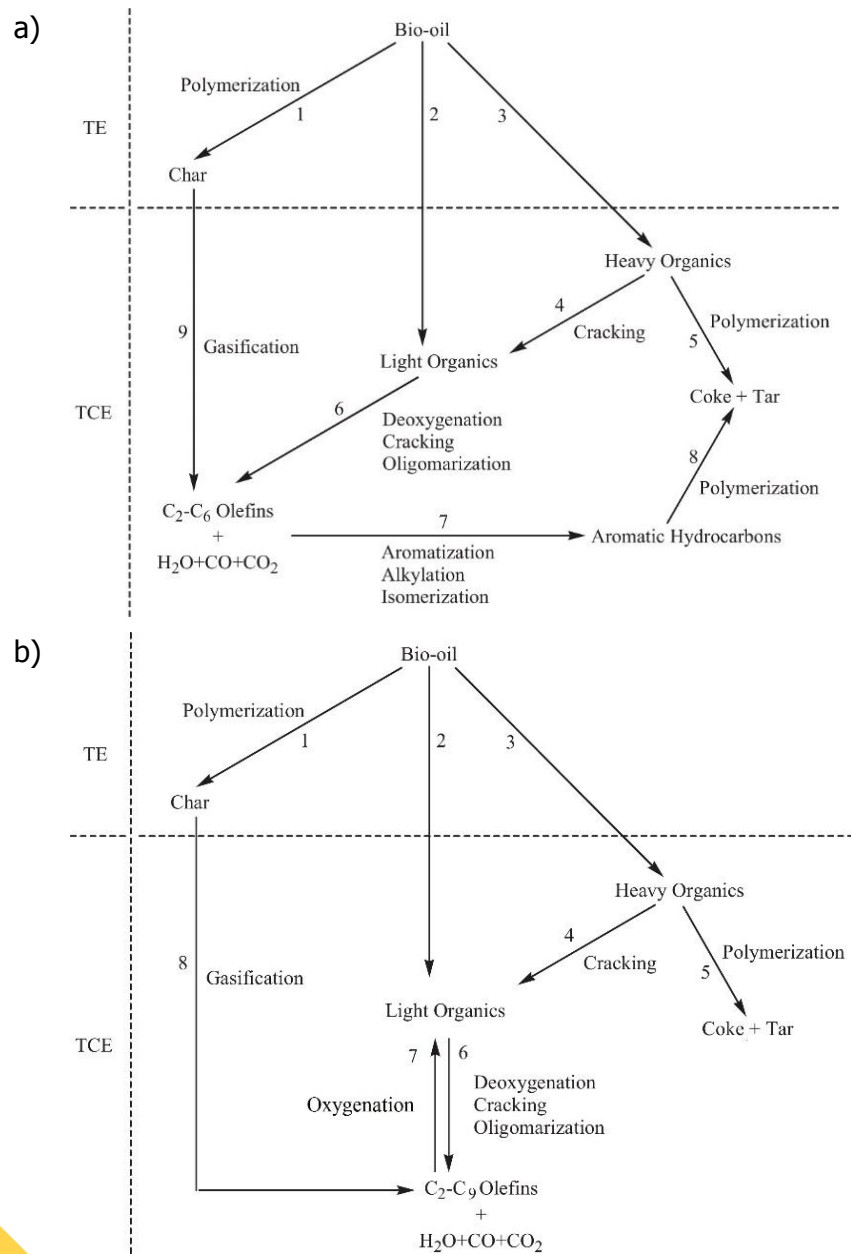
	Amount (wt.%)	Comment
<b>Aliphatic hydrocarbons</b>	0.5	Desired
Alkanes		
Alkenes		
Cyclic hydrocarbons		
<b>Aromatic hydrocarbons</b>	5.6	
Monoaromatic compounds		Desired
Polycyclic aromatic hydrocarbons		Undesired
<b>Oxygenated compounds</b>		
Aldehydes	10.9	Undesired
Ketones	36.6	Undesired
Carboxylic acids and Esters	10.4	Undesired
Furans	2.5	Valuable
Ethers	2.2	-
Alcohols	5.3	Valuable
Phenols	10.9	Valuable
Unidentified	14.7	

The challenge in catalyst development is to design a deoxygenation catalyst that selectively removes problematic oxygenates in the bio-oil and thus in one step improves the physical properties of the bio-oil and at the same time makes it suitable as a fuel precursor/additive. The oxygen may be given off by dehydration, decarbonylation and decarboxylation leading to the formation of water, CO and CO<sub>2</sub>, respectively. Selective removal of carboxylic acids (formic, acetic acids) by decarboxylation will decrease the acidity of bio oil. Selective deoxygenation of organic fractions (aldehydes, unsaturates, etc), which undergo easy condensation/oligomerisation reactions, can help to help the stabilisation of the oil. To assess the best mode of de-oxygenation of the vapors, basic calorific value calculations were done based on the elemental formula (C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>) for bio-oil (see **Figure 2**). Calculation shows that 75% de-oxygenation via decarboxylation will improve the heating value of the bio-oil from 19.4 MJ/Kg to 34.1 MJ/Kg. It is evident from these calculations that the decarboxylation is the preferred route for de-oxygenation in comparison to dehydration and decarbonylation as decarboxylation allows retention of hydrogen in bio-oil, maximizes oxygen removal with minimal carbon loss and thereby increases heating value, decreases the aromatics formation, minimizes the water content of the bio-oil, and decreases its hydrophilicity.



**Figure 2:** Effectiveness of different modes of de-oxygenation to improve the heating value of bio-oil

As bio-oil contains large molecules derived from lignin, the use of cracking catalysts could selectively crack the lignin-derived compounds in pyrolysis products. Preventing polymerization will also be beneficial for downstream upgrading processes because the high molecular weight fraction needs to be cracked for fuel production. Catalytic cracking is well known in petroleum refinery and used to break down the large and complex hydrocarbon molecules into smaller and simpler ones, since the heavy lignin derivatives also contain a high proportion of oxygen. Reducing these compounds and simultaneously increasing hydrocarbons yields would decrease the oxygen content of the bio-oil, thus increase its heating value. The catalytic cracking of hydrocarbons is believed to be a chain reaction that follows the carbenium ion theory developed by Whitmore et al., and the mechanism includes three steps: initiation, propagation, and cracking [21, 22]. In the cracking of hydrocarbons, the main reaction routes involve C–C bond scission [23]. While in the case of biomass pyrolysis, the cleavage of C–OH bonds (dehydration) or C–CO(OH) bonds (decarbonylation or decarboxylation) becomes also important due to the carbohydrate and phenolic components of cellulose, hemicellulose and lignin from the lignocellulosic biomass. Thus a catalyst for biomass pyrolysis should catalyze several reactions as dehydration, decarboxylation, decarbonylation, (de)alkylation, cracking, isomerization, cyclization, oligomerization and aromatization. Several types of catalyst have been studied for online catalytic pyrolysis of biomass, such as zeolites (ZSM-5, Y, Mordenite and Beta), silica-alumina, activated alumina, mesoporous aluminosilicates, alkali metals, alkaline earth metals. Adjaye & Bakhshi et al. has proposed a reaction pathway for the conversion of bio-oil over zeolite and silica-alumina catalysts (**Figure 3**) [20], the specific catalytic function of various catalysts can alter the product yields and selectivity, thus affecting the composition of bio-oil and its physical and chemical properties. In this research work, the catalyst performance has been studied based on the criteria outlined in this chapter.



**Figure 3:** Reaction pathways for the conversion of bio-oil over zeolite (a) and silica-alumina (b) catalysts (TE: thermal effect; TCE: thermo-catalytic effect) [20]

### 1.3 Objective and outline of thesis

The focus of this thesis work is to develop a catalyst and a process that can selectively de-oxygenate the bio-oil and produce a fuel precursor, which can be readily refined using conventional fuel upgrading technologies. In this thesis work, modified zeolites and sodium base catalyst are applied for online catalytic pyrolysis in different modes, in-situ and ex-situ, and the performance of different catalysts is investigated for different kinds of biomass sources either wood alone or triglycerides rich wood.

Chapter 2 contains a literature review to compare the performance of catalysts used for online catalytic pyrolysis in different modes of application, in-situ and ex-situ, and with respect to the scale of the experimental setup i.e. analytical scale, bench scale and pilot scale.

Chapter 3 is a study of modified zeolites in a lab scale unit. Furthermore an online pyrolysis vapor fractionation is presented as a tool to tailor the desired properties of bio-oil.

Chapter 4 presents the performance of a novel alumina-supported sodium carbonate catalyst with two different reactor systems. The effect of the catalysts on the quality of the bio-oil has been reported.

Chapter 5 is focused on the production of hydrocarbon rich bio-oil by catalytic pyrolysis of triglycerides contained biomass, a vegetable-oil-impregnated wood and triglycerides inherited jatropha cake.

Chapter 6 presents the effect of a  $\text{Na}_2\text{CO}_3$  catalysts system on the primary reaction kinetics of biomass pyrolysis in a novel thermogravimetric vortex reactor system.

Chapter 7 concludes this thesis work with recommendations.

It is noted that chapter 2-5 are published in peer reviewed scientific journals.





## 1.4 References:

1. Henrich, E., et al. *The status of the FZK concept for biomass gasification*. in *2nd European Summer School on Renewable Motor Fuels*. 2007. Poland.
2. Van de Beld, B., E. Holle, and J. Florijn, *The use of pyrolysis oil and pyrolysis oil derived fuels in diesel engines for CHP applications*. *Applied Energy*, 2013. **102**: p. 190-197.
3. Sturzl, R. *The commercial co-firing of RTP bio-oil at the Manitowoc Public Utilities power generation station*. 1997; Available from: <http://www.ensyn.com>.
4. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil*. *Energy & Fuels*, 2004. **18**(2): p. 590-598.
5. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. *Biomass and Bioenergy*, 2012. **38**(0): p. 68-94.
6. Bridgwater, A.V., D. Meier, and D. Radlein, *An overview of fast pyrolysis of biomass*. *Organic Geochemistry*, 1999. **30**(12): p. 1479-1493.
7. Jahirul, M., et al., *Biofuels Production through Biomass Pyrolysis —A Technological Review*. *Energies*, 2012. **5**(12): p. 4952.
8. Bridgwater, A.V., *Renewable fuels and chemicals by thermal processing of biomass*. *Chemical Engineering Journal*, 2003. **91**(2–3): p. 87-102.
9. Katikaneni, S.P.R., J.D. Adjaye, and N.N. Bakhshi, *Performance of Aluminophosphate Molecular Sieve Catalysts for the Production of Hydrocarbons from Wood-Derived and Vegetable Oils*. *Energy & Fuels*, 1995. **9**(6): p. 1065-1078.
10. Bridgwater, A.V. and G.V.C. Peacocke, *Fast pyrolysis processes for biomass*. *Renewable and Sustainable Energy Reviews*, 2000. **4**(1): p. 1-73.
11. Yaman, S., *Pyrolysis of biomass to produce fuels and chemical feedstocks*. *Energy Conversion and Management*, 2004. **45**(5): p. 651-671.
12. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users*. *Energy & Fuels*, 1999. **13**(4): p. 914-921.
13. Piskorz, J., D.S. Scott, and D. Radlein, *Composition of Oils Obtained by Fast Pyrolysis of Different Woods*, in *Pyrolysis Oils from Biomass*. 1988, American Chemical Society. p. 167-178.
14. Scholze, B., C. Hanser, and D. Meier, *Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl groups, and <sup>13</sup>C-NMR*. *Journal of Analytical and Applied Pyrolysis*, 2001. **58–59**: p. 387-400.
15. Oasmaa, A. and E. Kuoppala, *Fast Pyrolysis of Forestry Residue. 3. Storage Stability of Liquid Fuel*. *Energy & Fuels*, 2003. **17**(4): p. 1075-1084.
16. Bridgwater, A.V., *Catalysis in thermal biomass conversion*. *Applied Catalysis A: General*, 1994. **116**(1–2): p. 5-47.
17. Maggi, R. and B. Delmon, *Characterization and upgrading of bio-oils produced by rapid thermal processing*. *Biomass and Bioenergy*, 1994. **7**(1–6): p. 245-249.
18. Elliott, D.C., *Historical Developments in Hydroprocessing Bio-oils*. *Energy & Fuels*, 2007. **21**(3): p. 1792-1815.



19. Mortensen, P.M., et al., *A review of catalytic upgrading of bio-oil to engine fuels*. Applied Catalysis A: General, 2011. **407**(1–2): p. 1-19.
20. Adjaye, J.D. and N.N. Bakhshi, *Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts*. Fuel Processing Technology, 1995. **45**(3): p. 161-183.
21. Whitmore, F.C., *Mechanism of the Polymerization of Olefins by Acid Catalysts*. Industrial & Engineering Chemistry, 1934. **26**(1): p. 94-95.
22. Watson, B.A., M.T. Klein, and R.H. Harding, *Catalytic cracking of alkylbenzenes: Modeling the reaction pathways and mechanisms*. Applied Catalysis A: General, 1997. **160**(1): p. 13-39.
23. Wojciechowski, B.W. and A. Corma, *Catalytic cracking: Catalysts, chemistry, and kinetics*. 1986. Medium: X; Size: Pages: 248.



## CHAPTER 2:

# An overview of catalysts in biomass pyrolysis for production of biofuels<sup>1</sup>

**Abstract:** In-situ catalytic pyrolysis of biomass has been extensively studied in recent years for cost-competitive production of high quality bio-oil. To achieve that, numerous catalysts have been studied to facilitate in-situ upgrading of low-grade condensable vapors (bio-oil) by converting oxygenated compounds and large-molecule species. In this review, these catalysts are categorized in different families and a systematic evaluation of the catalyst effects on pyrolysis products and their characteristics is carried out with respect to the scale of the experimental setup. Among these catalysts, microporous zeolites are considered as most promising in terms of performance and the potential to tailor the desired bio-oil properties. More specifically, the prominent advantages of zeolites include efficient deoxygenation and molecular weight reduction of the resultant bio-oil, while the main drawbacks are decreases in the yield of bio-oil's organic phase and catalyst deactivation by coke deposition. In addition to the zeolite-based catalysts, other catalysts including mesoporous aluminosilicates, a widely-applied class of catalysts used for deoxygenation of bio-oil as well as alkaline compounds are also reviewed and discussed herein. The research on the latter has not been extensive but the preliminary results have revealed their potential for deoxygenation of bio-oil, production of hydrocarbons, and reduction of undesired compounds. Nevertheless, these catalysts need to be further investigated systematically. Overall, further development of dedicated catalysts for selective deoxygenation and cracking of bio-oil would be essential for scaling up the existing pyrolysis technologies to achieve commercial production of biofuels through pyrolysis.

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## 2.1 Microporous zeolites for catalytic pyrolysis of biomass

### 2.1.1 Catalytic pyrolysis of biomass model compound and biomass at analytical scale

Solid acid zeolites have been used predominantly for the catalytic pyrolysis of biomass, and zeolites have been considered for the post pyrolysis upgrading of the bio-oil since the early eighties. Zeolites are typical catalysts used in petroleum industry for upgrading low-octane components in the gasoline boiling range, as well as isomerising low-octane linear olefins to high-octane branched olefins [1]. octane linear olefins to high-octane branched olefins (Sadeghbeigi, 2000). The advantages of applying zeolites for biomass pyrolysis are attributed to their relatively low price and the knowledge gained over decades from their applications in chemical industries. Zeolites represent a well-defined class of crystalline aluminosilicate minerals whose three-dimensional structures are derived from coordination polyhedral of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  [2]. The critical properties of zeolites are their structure, Si/Al ratio, particle size, and nature of the (exchanged) cation. These primary structure/composition factors influence its acidity, thermal stability, and overall catalytic activity. The acidic properties (Brønsted sites) of zeolites are dependent on the method of preparation, the form and the temperature of dehydration, and the Si/Al ratio. The structures of common zeolites are tabulated in **Table 3** [3].

**Table 3:** Channel structures of common zeolites [3]

Zeolites	Channel structure
ZSM-5	3-Dimensional pore system; straight 10 member-ring $5.2 \times 5.7 \text{ \AA}$ channels connected by sinusoidal $5.3 \times 5.6 \text{ \AA}$ channels. Intersection cavity: $9 \text{ \AA}$
Mordenite	2-Dimensional pore system; straight 12-ring $7.0 \times 6.5 \text{ \AA}$ channels connected by short alternating 8-ring channels ( $3 \text{ \AA}$ )
Beta	3-Dimensional pore system; 12-ring channel in c direction with pores $7.6 \times 6.4 \text{ \AA}$ plus two 12-ring channels in a direction perpendicular to c-direction with pores $7.6 \times 6.4 \text{ \AA}$ and $5.5 \times 5.5 \text{ \AA}$
Y	3-Dimensional pore structure; circular 12 member-ring $7.4 \text{ \AA}$ windows connecting spherical $11.8 \text{ \AA}$ cavities (super cages)

Among different zeolite-based catalysts, ZSM-5 is considered to be an effective catalyst for cracking, deoxygenation, and formation of aromatic hydrocarbons [4-12]. ZSM-5 was initially developed for the conversion of methanol and light alcohols to gasoline in well-recognized methanol-to-gasoline (MTG) process. Promising catalytic performance of ZSM-5 is due to its unique shape selectivity. Hoff et al. investigated the effect of the physicochemical properties of ZSM-5 catalyst on the yield of aromatic compounds produced by fast pyrolysis of cellulose. They found that aromatics formation was strongly dependent on the crystallinity and accessibility of framework aluminum sites. [13].

It is worth mentioning that ZSM-5 has also been extensively studied for catalytic deoxygenation of oxygenated organic compounds [14, 15]. For example, transformation of alcohols, phenols, aldehydes, ketones, and acids, as the prominent components of bio-oil, was investigated over an HZSM-5 zeolite by Gayubo et al. and these model compounds were shown to be significantly different in terms of reactivity and coke formation [12, 16]. In the continuation of this work, Gayubo et al. treated a mixture of acetone, acetic acid, acetaldehyde, phenol, 2-butanol, and methanol over HZSM-5, and obtained a high proportion of olefins, butenes, propene, aromatics, and paraffins [17]. While a mixture of oxygenates containing 2-methoxyphenol and furfural showed low reactivity in the presence of HZSM-5 which could be ascribed to the formation of carbonaceous residues on the catalyst. They also argued that, aldehydes, phenols, and furfural could undergo severe thermal degradation resulting in the formation of carbonaceous deposits on the catalyst, and consequently, an intense deactivation of the catalyst.

Carlson et al. also evaluated different zeolite-based catalysts in a pyroprobe analytical pyrolyzer. A diverse range of aromatics increasingly formed that could lower the pH value of the bio-oil from the catalytic pyrolysis of glucose, xylitol, cellobiose, and cellulose [18, 19]. The product selectivity was dependent on both the pore size of the catalyst and the nature of the active sites. High heating rate and high catalyst loadings favored the production of aromatic over coke formation and thermally stable oxygenates formed at low catalyst-to-feed ratio. Carlson et al. concluded that the reaction conditions and catalyst properties are important to maximize the desired product selectivity.

Activated alumina has relatively high activity which is comparable to that of dolomite [20]. Activated alumina consists of a series of nonequilibrium forms of partially hydroxylated aluminum oxide, and can be found in several minerals. The porous solid structure of activated alumina can be produced by heating (calcining) the hydrous alumina precursor to drive off the hydroxyl groups [3]. Samolada et al. studied the comparative performance of alumina and HZSM-5 in a packed bed catalyst reactor with a synthetic bio-oil [9], alumina retained the high liquid yield but it could not contribute to any considerable improvements of the liquid product composition. HZSM-5 completely converted the undesirable carbonyls, to hydrocarbons with a simultaneous decrease in organic liquid yield and an increase in yield of water. Organic liquid produced contained significant amounts of aromatic hydrocarbons with Benzene, toluene, methyl-substituted benzenes, and indenenes being dominant.

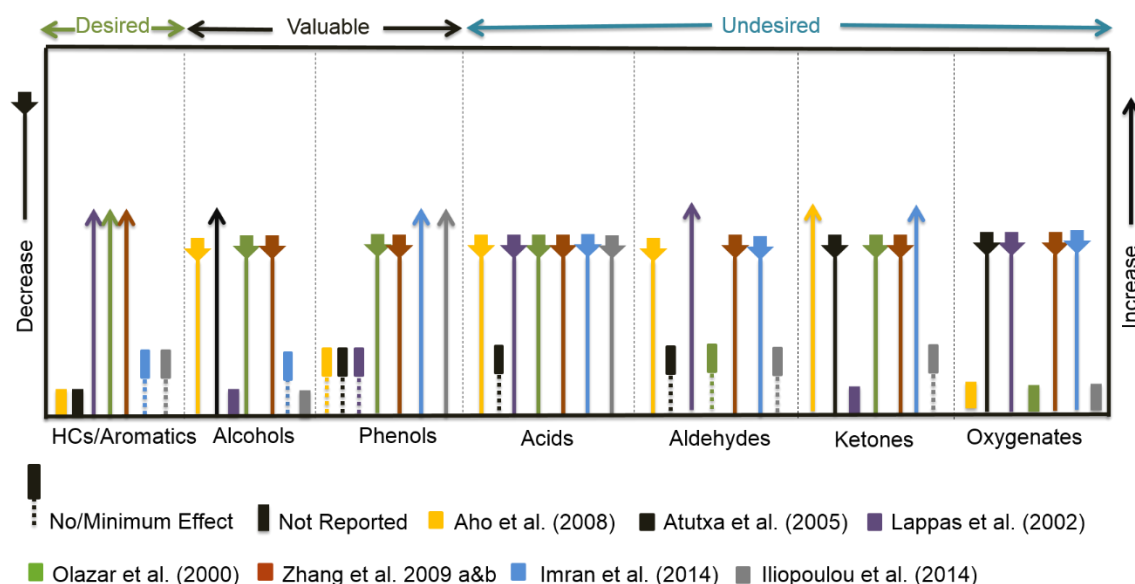
French et al. performed catalytic upgrading of cellulose, lignin, and wood pyrolysis vapors using modified commercial and laboratory synthesized zeolite catalysts in a tubular quartz micro-reactor [21]. Compared to larger-pore zeolites, alumina and Y zeolite, metal substituted ZSM-5 showed high activity for converting oxygenated pyrolysis vapors to hydrocarbons, and all the primary pyrolysis products except water and carbon oxides were converted mostly to hydrocarbons and coke. Karnjanakom et al. used metal (Zn, Ce or Ni) modified alumina for in-situ catalytic upgrading of bio-oil from the fast pyrolysis of sunflower stalk in a fixed bed reactor. Metal loading of alumina showed high activity and selectivity for upgrading of oxygenated compounds in the bio-oil to aromatic hydrocarbons, especially benzene, toluene and xylene and Ni/Al<sub>2</sub>O<sub>3</sub> yielded the highest amount of hydrocarbons in the bio-oil [22]. Thangalazhy-Gopakumar et al. and Lisa et al. reported increases in liquid hydrocarbons yields by increasing the ZSM-5 loading in an

analytical pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) reactor [23, 24]. In addition to that, it should be noted that the preparation method used for zeolite-based catalysts could also play a key role in the properties of the resultant catalyst. For instance, the porous ZSM-5 prepared by desilication (treatment with NaOH) showed increased aromatic yields in catalytic pyrolysis of beech wood compared with the parent ZSM-5 [25]. Mullen et al. found increase in production of aromatic hydrocarbons from cellulose, cellobiose and lignin using iron-modified HZSM-5 in a microscale pyrolysis reactor coupled with GC/MS [26]. Fischer et al. also found a considerably larger amount of aromatic hydrocarbons formed with ZSM-5 for pyrolysis of spent coffee grounds in both a fixed bed reactor and a pyroprobe. This effect was attributed to de-carbonylation reactions as the increased formation of aromatics with ZSM-5 was accompanied by a slight increase in the carbon oxide. [27]. Pattiya et al. found ZSM-5 the most active catalyst for treatment of cassava rhizome biomass pyrolysis vapors in an analytical Py-GC/MS [28, 29]. ZSM-5 enhanced the formation of aromatic hydrocarbons and phenols, decreased the amounts of oxygenated lignin-derived compounds, and reduced the formation of carbonyl compounds. The aromatic production of ZSM-5 was linked to its acidity together with its shape selectivity. A drawback of ZSM-5 was the increased formation of acetic acid that can lower the pH value of the liquid. Engtrakul et al. also found that acidity of ZSM-5 has strong influence on the selectivity of aromatic products for upgrading of pine pyrolysis vapors in a micro-furnace pyrolyzer [30]. Increasing the acidity of zeolite resulted in a reduction of alkylated aromatics, and increment in the formation of unsubstituted and polycyclic compounds. This phenomenon was attributed to the changes in rate of cyclization and alkylation reaction. Sun et al. found superior performance of Fe/ZSM-5 over ZSM-5 for catalytic fast pyrolysis of biomass using a Py-GC/MS [31]. Fe/ZSM-5 showed superior activity for conversion of oxygenates and formation of monocyclic aromatic hydrocarbons with increased yields of aromatic hydrocarbons in the bio-oil. Liang and Xiang et al. investigated the effects of transition metal (Zn, Co, and Ni) modified ZSM-5 for in-situ upgrading of pyrolysis vapors of rice straw and found a pronounced effect of transition metal modified ZSM-5 to improve the compound selectivity in the bio-oil and to increase the yield of bio-oil [32, 33].

### **2.1.2 In-situ catalytic pyrolysis of biomass at bench scale**

Several researchers have studied different zeolite catalysts for in-situ catalytic biomass pyrolysis in bench scale experimental setups. **Table 4** summarizes the influence of selected catalysts on product distribution of biomass pyrolysis. Despite the differences in biomass type and other operational parameters, the results obtained in these studies are remarkably consistent. For example, all of these investigations have confirmed that zeolite catalysts reduced the organic liquid yield compared to non-catalytic experiments, while water and gas yields were increased in general. Moreover, the majority of these studies have argued that coke formation was as a major deoxygenation route. For instance, Nyguyn et al. reported that the coke deposited on the catalyst had a high oxygen content of up to 41.5 wt.% [34]. Overall, there is a consensus in the results and the slight differences could be attributed to differences in catalyst/vapor contact associated with the different reactor types, type of biomass fed, catalyst-to- biomass ratio, and the other operational parameters, e.g., reactor temperature and vapor gas flow rate, etc.

As the characteristics of boil-oil, especially yield of oxygenated components and chemical composition of bio-oil, are of main interest for fuel application as well as for handling and storage properties, many researchers have described the effect of zeolite catalysts on bio-oil chemical composition in detail. A summary of the effects of zeolite on bio-oil chemical composition as reported in selected studies is presented in **Figure 4**. Aho et al. found that zeolite structure significantly affected the chemical composition of pine wood pyrolysis liquid using acidic zeolite catalysts, proton forms of Beta, Y, ZSM-5, and Mordenite in a fluidized bed reactor [35]. Among the zeolite-based catalysts used, ZSM-5 produced the hydrocarbons and phenolic compounds and was lighter than the aqueous phase. Cobalt addition significantly increased the formation of CO<sub>2</sub> compared to CO and was suggested to have strongly enhanced aromatization reactions.



**Figure 4:** Summary of zeolites effect on chemical composition of the bio-oil for in-situ catalytic pyrolysis.

Jae et al. also reported ZSM-5 very stable through repeated reaction/regeneration cycles in a fluidized bed reactor, and high amount of aromatics was achieved [36]. Yildiz et al. showed, after successive regenerations, ZSM-5 retained the sufficient activity in producing the target chemical components for catalytic pyrolysis of pine wood in a lab-scale setup, fresh ZSM-5 formed the aromatics, completely converted the aldehydes and sugars, and reduced the acids and ketones [37]. In a recent work, Yildiz et al. studied the catalytic pyrolysis of pine wood with various metal doped ZSM-5 and  $\gamma$ -alumina in same bench-scale auger reactor [38]. All the catalysts enhanced the water and coke formation at the expense of bio-oil yield. However, some of the catalysts remarkably improved the quality of bio-oil, especially the acidity of bio-oil was significantly decreased with an increased deoxygenation. The lower redox-metal containing acidic catalyst and freshly calcined metal doped basic mixed-metal oxide catalysts showed the best performance. Paasikallio and Agblevor et al. also reported more aromatics compounds and less sugar compounds obtained in bio-oil for catalytic fast pyrolysis of forest thinnings

in a bench-scale bubbling fluidized bed reactor, and bio-oil had considerably lower oxygen contents [39]. In the same bench-scale bubbling fluidized bed reactor, Mante and Agblevor et al. examined ZSM-5 as a co-catalyst to Y-zeolite based FCC catalyst ((Fluid Cracking Catalyst) for catalytic pyrolysis of hybrid poplar [40], the addition of ZSM-5 to the FCC catalyst increased organic liquid fraction and decreased coke/char and gas yields, and enhanced the formation of aromatic compounds and decreased aliphatic hydrocarbons. Lappas et al. [41] used FCC and a ZSM-5 based FCC catalyst (zeolite content: 10 wt %) for catalytic flash pyrolysis of lignocellulosic biomass in a lab pilot scale circulating fluid bed reactor unit with continuous solids regeneration. Both catalysts reduced the oxygenated compounds, and increased the hydrocarbons in the bio-oil. ZSM-5 produced more carbonyls, while the yields of acids, HCs, phenols and heavy oxygenates were not significantly changed

Bertero et al. reported similar finding using FCC catalyst in a bench scale integrated fixed bed pyrolysis-conversion reactor for pyrolysis of soybean shell and pine saw dust. Yield of hydrocarbon in the bio-oil was increased four times compared to the non-catalytic bio-oil, with a higher selectivity to hydrocarbons in the gasoline range with more olefins and less aromatic [42]. Lately, Iliopoulou and Lappas et al. studied the cobalt promoted ZSM-5 in same pilot scale circulating fluid bed reactor setup for in situ upgrading of lignocellulosic biomass pyrolysis vapors [43]. Co-promoted ZSM-5 resulted in the formation of a three phase bio-oil than the usual two phase (aqueous and organic phases) catalytic bio-oil, the third phase consisted mainly of aromatic hydrocarbons and phenolic compounds and was lighter than the aqueous phase. Cobalt addition significantly increased the formation of CO<sub>2</sub> compared to the CO and suggested to strongly enhance aromatization reactions. In a previous work, Iliopoulou and lappas et al. reported similar effect with Ni-promoted ZSM-5, and aromatics and phenols were increased in the bio-oil [44]. Hernando and Feroso et al. studied the effect of Mg and Zn oxides modified ZSM-5 in a bench scale downdraft fixed-bed reactor for the catalytic fast-pyrolysis of eucalyptus woodchips [45, 46]. Compared to non-catalytic fast pyrolysis, the use of catalysts caused a decrease in the bio-oil yield due to enhanced formation of gases and formation of coke on the catalyst. However, the use of the catalyst produced a higher quality bio-oil with lower oxygen content and higher heating value. The modified ZSM-5 (with MgO and ZnO) tailored the catalyst activity to avoid an excessive cracking of the bio-oil and resulted in a higher yield of the organic compounds in the bio-oil (with increased yield of monocyclic aromatics and decreased yield of coke). MgO-modified HZSM-5 achieved deeper deoxygenation and produced a bio-oil with higher energy value probably due to the adequate balance of Lewis acid and basic sites as a result of MgO addition.

Olazar et al. achieved considerable deoxygenation of bio-oil through catalytic pyrolysis of sawdust in a conical spouted bed reactor over HZSM-5 and found an increase in production of non-oxygenate hydrocarbons within the C<sub>5</sub> - C<sub>10</sub> range as well as aromatics [47]. In a later investigation, Atutxa et al. reported less oxygenated bio-oil produced from saw dust using HZSM-5 in a similar conical spouted bed reactor, though excessive coke formation on the catalyst was observed [48]. For pyrolysis of corncob in a fluidized bed reactor over HZSM-5 and FCC, Zhang et al. applied multi-stage condensation by collecting three different liquid fractions: heavy, light, and aqueous [49, 50]. The light oil fraction showed a considerable decrease in oxygen content and showed a remarkable increase in aromatic hydrocarbons content, while all other types of compounds were decreased. FCC reduced the amount of multifunctional components of phenols that are considered as likely



polymerization precursors in the bio-oil. Such a remarkable improvement in the quality of light oil fraction could be attributed to the combined effect of catalyst application and multi-stage condensation. Imran et al. reported dramatic improvement in quality of catalytic bio-oil with a sodium modified alumina. They obtained a highly deoxygenated bio-oil through in-situ catalytic fast pyrolysis of biomass in a bench scale entrained flow reactor setup. Pyrolysis liquid showed a spontaneous separation into aqueous phase and organic phase (bio-oil). The undesired compounds in the bio-oil, i.e., acids, aldehydes, and sugars were completely converted and there were significant increases in the yields of phenols and ketones. The bio-oil had a very low oxygen content (16.4 wt.%), water content as low as. Overall, oxygenated compounds in bio-oil have been found to decrease in all the above-mentioned studies and undesired compounds were reduced in most cases using zeolites during *in-situ* catalytic biomass pyrolysis. Moreover, zeolites could generally result in significant reduction of acids which are responsible for low pH values of bio-oils. Aldehydes, contributors to poor stability of bio-oil, were also either reduced or unaffected in all the reported studies except that of Lappas et al (2002). who claimed an increase in aldehydes content. The majority of these studies did not find any positive effects of zeolites on alcohol compounds in the bio-oil.

It should be noted that although all these studies (carried out at bench scale reactor systems) revealed positive effects of HZSM-5 and FCC catalysts on chemical composition of bio-oils, the improvements were not as pronounced as claimed at micro and analytical scaled studies (section 2.1.1.). This could be explained by the fact that most of micro and analytical scale studies were conducted with packed bed type catalyst systems and at relatively higher catalyst-to-biomass ratios. In another word, the less pronounced effect of HZSM-5 at bench scale units could be attributed to poor catalyst/vapor contact in fluidized bed type reactor systems and the lower catalyst-to-biomass ratios employed.

**Table 4:** Summary of zeolites effect on biomass pyrolysis products yields for in-situ catalytic pyrolysis

Catalyst	Feed	Reactor type	Bio-Oil	Water	Gas	Char	Coke	Ref.
<b>HZSM-5</b>	Pine Wood	Fluidized bed reactor	-	+	n/e	-	+	[35]
<b>HZSM-5 &amp; FCC</b>	Lignocell	Circulating fluidized bed reactor	-	+	+	+	+	[41]
<b>Co- ZSM-5</b>	Lignocell	Circulating fluidized bed reactor	-	n/e	+	+	+	[43]
<b>HZSM-5</b>	forest thinnings	Bubbling fluidized bed reactor	-	n/e	+	n/e		[39]
<b>Co- ZSM-5 Ni-ZSM-5</b>	Lignocell	Circulating fluidized bed reactor	-	+	+	+	+	[44]
<b>HZSM-5</b>	Sawdust	Conical spouted bed reactor	-	+	+	-	+	[48]
<b>FCC</b>	Lignocell	Fluidized bed reactor	-	+	+	+	+	[51]
<b>HZSM-5</b>	Sawdust	Fluidized bed reactor	-	+	+		+	[47]
<b>HZSM-5 &amp; FCC</b>	Corncob	Fluidized bed reactor	-	n/e	+	-	+	[50]
<b>Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub></b>	Lignocell	Entrained flow reactor	-	+	+	+		[52]

*+ and – signs indicate the increase and decrease in yield respectively, n/e indicates no or minimum effect, and blank column indicates the results are not reported.*

### 2.1.3 Ex-Situ catalytic pyrolysis of biomass at bench scale

*Ex-situ* catalytic treatment of pyrolysis vapors over a packed bed of catalyst could address the many problems generally associated with *in-situ* catalytic pyrolysis. More specifically, since the *ex-situ* catalytic reaction is carried out inside a separate reactor, a more appropriate catalyst/vapor contact through higher catalyst-to-biomass ratios could be achieved. A considerable number of studies have been performed on *ex-situ* catalytic pyrolysis of biomass at bench scale in packed zeolite-based catalyst reactor systems. A summary of the effects of zeolites on pyrolysis products and chemical composition of bio-oil during *ex-situ* catalytic treatment of bio-oil vapors is presented in **Table 5**. As shown, all these investigations reported decreases in organic liquid yield with high levels of deoxygenation and increases in water, gas, and coke yields. For instance, through upgrading of the fast pyrolysis vapors of olive residue in a two stage packed bed reactor using various catalysts (i.e., ZSM-5, H-Y, and natural zeolite (N-Z)), Putun et al. found reductions in oxygenated species of bio-oil [53]. More specifically, the authors claimed that highly oxygenated polar groups and asphaltenes were dramatically decreased while alkanes and alkenes with long chains were effectively converted to lower molecular weight hydrocarbons and the amounts of aliphatics, aromatics, and olefins were increased in the bio-oil. Similar findings were also reported in a series of previous studies in which ZSM-5, Y-type zeolites, and activated alumina were found effective for deoxygenation of bio-oil during *ex-situ* upgrading of biomass vapors in packed bed reactors leading to enhanced formation of single ring aromatics and PAHs [5, 10, 54, 55]. Williams and Nugranad et al. reported that the molecular weight distribution of bio-oil was decreased with ZSM-5. Stephanidis et al. also achieved enhanced formation of single ring and PAHs and significant deoxygenation of bio-oil produced by online vapor upgrading of lignocellulosic biomass pyrolysis vapors in a bench scale packed bed reactor of HZSM5 while the amount of acids, esters, aldehydes, ketones, and phenols were decreased [56].

Li et al. also reported improved generation of aromatic hydrocarbons in bio-oil with incorporating metal elements (Zr, CO, and Fe) on HZSM-5 for catalytic fast pyrolysis of sawdust in a vertical two-stage reactor [57]. Metal-modified HZSM-5 showed superior catalytic activity for bio-oil upgrading compared to the parent HZSM-5 and metal-modified HZSM-5 produced bio-oil containing up to 45% aromatic hydrocarbons. Recently, Li et al. performed pine wood pyrolysis in an auger reactor of 25 kg/h capacity and carried out immediate treatment of pyrolysis vapor in a packed bed reactor of ZSM-5 [58]. Accordingly, ZSM-5 achieved a significant deoxygenation of the bio-oil, considerably increased the aromatics and phenol, and effectively removed the oxygenated compounds (such as acids, alcohols, carbonyls and carbohydrates) from the bio-oil.

In spite of the attempts made to date, a detailed analysis of the chemical composition of bio-oil is still lacking. Nevertheless and based on the findings of the studies reported above, it could be deduced that zeolites packed bed systems are capable of efficient deoxygenation of bio-oil; enhanced formation of hydrocarbons/aromatics (i.e., the most desired compounds for fuel applications), and reduced formation of acids (i.e., the most undesired compounds in bio-oil). However, it should also be noted that packed bed reactor system is not a viable option to scale up for commercial applications due to difficulties in continuous regeneration of the catalyst compared to available commercial reactor systems, e.g., fluidized bed reactors.

**Table 5:** Summary of biomass pyrolysis products yields and bio-oil composition for ex-situ online upgrading of pyrolysis vapors over packed bed of zeolites.

Catalyst	Feed	Catalyst Reactor type	Bio-Oil	Water	Gas	Coke	HCs	PAHs	KETs	FURs	PHEs	ALCs	ACIDs	ALDs	Ref.
<b>ZSM-5</b>	Rice husk	Packed Bed	-	+	+	+									[10]
<b>ZSM-5, Y</b>	Wood	Packed Bed	-	+	+	+									[5, 54, 55]
<b>ZSM-5, H-Y and N-Z</b>	Olive residue	Packed Bed	-		+	+	+	+							[53]
<b>H-ZSM5</b>	Beech wood	Packed Bed	-	+	+	+	+	+	-	+	-	n/e	-	n/e	[56]
<b>H-ZSM-5</b>	Pine wood	Packed Bed	n/e	+	+		+		-		+	-	-	-	[58]

*+ and - signs indicate the increase and decrease in yield respectively, n/e indicates no or minimum effect, and blank column indicates the results are not reported (HCs-Hydrocarbons, PAHs-Poly Aromatic Hydrocarbons, KETs-Ketones, FURs- Furans, PHEs-Phenols, ALCs-Alcohols, ALDs-Aldehydes)*

## 2.2 Mesoporous aluminosilicates for catalytic pyrolysis of biomass

Mesoporous aluminosilicates have a uniform pore structure with pore sizes much larger than those of zeolites, high surface area, and moderate acidity compared to zeolites. Mesoporous aluminosilicates have gained a considerable deal of interest over last years for catalytic pyrolysis of biomass. This has been ascribed to the possibility of better matching the size of oligomers derived from the initial thermal degradation of biomass with the pore size of the catalyst. In better words, due to their large pore size and mild acidity, mesoporous aluminosilicates are expected to perform selective cracking and deoxygenation of large molecules as of lignin derived compounds without reducing organics yields significantly and without being quickly deactivated by coking [59]. Among these catalysts, MCM-41 exhibits extremely high surface areas (1000 m<sup>2</sup>/g and larger) and well-defined pore sizes with a relatively narrow pore size distribution in the range of 20–30 Å [60]. These attributes of MCM-41 materials could be obtained by controlling the preparation conditions, such as reaction temperature, reaction time, as well as the pH value [61]. Al-doped MCM-41 is the most predominantly studied aluminosilicate for catalytic biomass pyrolysis. Using a synthetic bio-oil, Samolada et al. found the catalytic activity of Al-doped MCM-41 comparable to that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. More specifically, the developed catalysts retained a high liquid yield but it could not contribute to any considerable improvements to the liquid product composition [9]. MCM-41 has been frequently used to catalyze specific reactions concerning bio-oil, such as the hydroxylation and alkylation of phenol [62, 63], oxidation and isomerization of hexane [64, 65], oxidation and dehydrogenation of hydrocarbons [66, 67], and hydrogenation of aromatics [68, 69].

Stephanidis et al. found catalytic effect of Al-MCM-41 somewhat similar to that of H-ZSM-5 for online upgrading of lignocellulosic biomass pyrolysis vapors in a small bench scale packed bed catalyst reactor but significantly higher coke was deposited on the catalyst [56]. Yields of acids, esters, aldehydes, ketones, and phenols were decreased while the single ring and poly aromatics concentrations were increased significantly using Al-MCM-41. Pattiya et al. compared ZSM-5, Al-MCM-41, and Al-MSU-F (a large pore size (>100 Å) aluminosilicate catalyst) for cassava rhizome pyrolysis vapor treatment using an analytical Py-GC/MS setup [28, 29]. Catalytic activities of Al-MSU-F and Al-MCM-41 were reportedly very similar to that of ZSM-5. Moreover, Al-MSU-F and Al-MCM-41 produced aromatic hydrocarbons and reduced the oxygenated lignin derivatives and phenols. Al-MSU-F produced more hydrocarbons, particularly benzene and xylenes, than Al-MCM-41. This phenomenon was attributed to the large pores of Al-MSU-F that would allow large pyrolysis molecules to enter, react, and exit the catalyst matrix. A drawback noticed with aluminosilicate was the increase in the formation of acids

### 2.2.1 Effect of different metal incorporation to mesoporous aluminosilicates

Since the first synthesis of MCM-41, much work has been carried out in incorporating various elements (Ni, Al, Co, Mo, Fe, Cu) together with silicon into the framework of MCM-41 to change the physicochemical properties of the material, especially to improve the acidic characteristics [70]. Some successful examples include the incorporation of Fe by

He et al. [71], Ti by Corma et al. [72, 73], V by Luan et al.[74], Cu by Wu et al. and Noreña-Franco et al.[62, 75], Zn by Selvaraj et al. [63]. It was found that the catalytic properties of mesoporous materials could be improved by the incorporation of these metal elements [76-78]. Bimetallic modified MCM-41 has also been investigated for the selective oxidation of styrene and benzene [79]. Antonakaou et al. found increased yields of hydrocarbons and PAHs for biomass pyrolysis over Cu–MCM-41, Fe–MCM-41 and Zn-MCM-41 in packed bed reactor [59]. Fe-MCM-41 and Cu-MCM-41 were best metal-containing catalysts for phenols production and Fe–MCM-41 reduced the carbonyl production. Only Cu-MCM-41 was successful to reduce acids and esters production, while Fe–MCM-41 and Zn-MCM-41 increased the alcohols yield. Cu- MCM-41 was also tested by resulting in the highest gas production and less water production compared to MCM-41. Adam et al. also found increase in desirable products for biomass pyrolysis over transition metal incorporated Al-MCM-41 [80, 81]. Independent of the Al content in the framework, the MCM-41 material shows a weak acidity comparable to amorphous aluminosilicates [82]. The presence of aluminium can improve the acidic and cracking characteristics of MCM-41[83]. It is worth mentioning that Si/Al ratio of Al- MCM-41 could also play an important role in the activity of the catalyst. More specifically, higher Si/Al ratios reportedly increased the organic phase of the pyrolysis bio-oil, while lower Si/Al ratios enhanced the conversion of bio-oil to gases and coke formation while also increased the yield of high value aromatic compounds [59, 84].

The catalytic effect of mesoporous aluminosilicates on biomass pyrolysis products yields and chemical composition of the bio-oil is summarized in **Table 6**. In conclusion, the performance of aluminosilicates in terms of the yields of biomass pyrolysis products would be relatively comparable to that of zeolites. More specifically, both tend to produce desirable compounds in the bio-oil and reduce the undesirable compounds in the bio-oil. However, compared to zeolites, larger pore sized aluminosilicates reduce catalyst deactivation as larger pores allow larger molecules, such as lignin-derived compounds, to enter, reform, and exit the catalyst with less chance of coke deposition.

**Table 6:** Summary of biomass pyrolysis products yields and bio-oil composition for online upgrading of pyrolysis vapors over packed bed of mesoporous aluminosilicates

Catalyst	Feed	Bio-Oil	Water	Gas	Char	coke	HCS	PAHs	KETs	FURs	PHEs	ALCs	ACIDs	CANs	Ref.
<b>Cu-MCM-41</b>	Lignocel	-	+	-		+	-	+	n/e	+	n/e	-		+	[59]
<b>Fe-MCM-41</b>	Lignocel	-	+	-		+	-	+	n/e	+	-	n/e		-	[59]
<b>Zn-MCM-41</b>	Lignocel	-	+	-		+	-	+	n/e	n/e	-	+		+	[59]
<b>Al-MCM-41</b>	Wood	-	+	n/e		+	+	+	+	+		-	-	-	[80, 81]
<b>Cu-Al-MCM-41</b>	Wood	n/e	n/e	+		+	+	+	+	+		-	-	-	[80, 81]
<b>Al-MCM-41</b>	Wood	-	+	n/e		+	+	+		+	n/e	-		+	[84]
<b>Al-MCM-41</b>	Beech wood	+	+	-	n/e	-	+	+	n/e	-	n/e	n/e	+		[56]

*+ and – signs indicate the increase and decrease in yield respectively, n/e indicates no or minimum effect, and blank column indicates the results are not reported (HCS-Hydrocarbons, PAHs-Poly Aromatic Hydrocarbons, KETs-Ketones, FURs- Furans, PHEs-Phenols, ALCs-Alcohols, CANs-Carbonyls)*

## 2.3 Alkaline compounds for catalytic pyrolysis of biomass

### 2.3.1 Catalytic effect of alkali metals on biomass pyrolysis

There are more than 19 inorganic species present in the biomass [85]. It is well known that some of these inorganic constituents of biomass including alkali metals and alkaline earth metals could act as catalyst during thermal degradation of biomass in pyrolysis process, determining the rate of thermal decomposition and yield of char [86]. Shafizadeh et al. found that the inorganic content in the biomass significantly affects the gas and char yields, and increasing the inorganic contents in the biomass accelerates the secondary cracking reactions to breakdown the higher molecular compounds to smaller ones [87]. Since the alkali and alkaline earth metals, especially some of them including potassium, sodium, calcium and magnesium, are indigenous to a variety of biomass relatively in abundance, attentions have early been paid to their catalytic effects from viewpoints of chemistry and application. Even at trace concentration (such as 0.1 wt% NaCl) of the mineral matter in biomass, the biomass pyrolysis product distribution is affected by mineral salts present in the biomass [88]. Extensive research has been carried out on the effect of alkali metals on the decomposition behavior of biomass under thermal degradation which in turn could affect the conversion of biomass during pyrolysis process. It has been shown that the main alkali metals of plant origin affecting pyrolysis degradation include sodium, potassium, and magnesium [86, 89, 90]. The cations of alkali metal in biomass affect the mechanism of thermal decomposition during fast pyrolysis and make the natural polymer chains via primarily fragmentation of the monomers [91]. In the last two decades, the effects of alkaline cations on the mechanism of pyrolysis of biomass have been more fully explored, and in particular, several workers have demonstrated the effects of deliberate addition of various alkaline and metallic cations to the biomass and of different pretreatments especially on the bio-oil yields and compositions. Raveendran et al. argued that the cations would exert more influence on the catalytic pyrolysis of biomass compared to their anion counterparts [89]. Pattiya and Bridgewater found that alkali metals present in cassava rhizome reduced bio-oil yield and addition of ash to biomass adversely affected the bio-oil yields, while the reduction of alkali metals by water washing showed an increase in the bio-oil yield [29].

It is well evident that alkali metals are strongly favorable for the formation of low molecular weight compounds by conversion of levoglucosan in biomass pyrolysis, Fahmi et al. found higher levoglucosan yield and the lower hydroxyacetaldehyde yield in a Pyro-GC/MS when alkaline metal content of biomass was decreased by washing [92]. Liden et al. reported the similar results for thermal degradation of cellulose and found that high levels of alkali metals favors fragmentation (ring scission) producing lower molecular weight compounds such as hydroxyacetaldehyde, while lower alkali metal contents favors the de-polymerisation resulting in higher molecular weight compounds such as levoglucosan and beta-d-fructose [90].

It is believed that wet impregnated alkali metal can affect the primary decomposition reaction and can control the products nature of biomass thermal degradation. Blasi and Galgano investigated the catalytic pyrolysis of wet impregnated alkali compounds (NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, and NaCl) onto the wood in a fixed-bed reactor, alkali compounds lowered the organics yield in the liquid and increased the yields of char, gases



and water [93-95]. Alkali compounds impregnation lowered the temperature of wood decomposition and time of conversion; these effects were enhanced by increasing the basicity of alkali compound. [96]. In a similar work, conducting catalytic pyrolysis of fir wood in a packed-bed reactor, higher concentration of KOH impregnated onto the wood lowered the decomposition temperatures of wood and increased the production of char, water, and CO<sub>2</sub> at the expense of organics in the liquid [97]. Jun et al. found the similar effect using Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaCl, Na<sub>2</sub>SiO<sub>3</sub> as a catalyst for biomass pyrolysis and sodium compounds made devolatilization occur at lower temperature regions and effect was higher with higher basicity. Higher amount of KOH increased the yields of furfuryl alcohol, some carbohydrates and phenols. Jensen et al. and Nowakowski et al. also observed that the potassium impregnation onto wheat straw and short rotation willow coppice enhanced the yields of gaseous product of the slow pyrolysis, with an increase in the yields of char [98, 99]. Raveendran et al. also reported increase in char for pyrolysis of KCl or K<sub>2</sub>CO<sub>3</sub> impregnated biomass samples [89] .

In practical application, wet impregnation of alkali metals pose technical and economic challenges and physical mixing of alkali metals is an easy and economical way for their implementation in catalytic pyrolysis of biomass. Physically mixed alkali metals are less likely to influence primary decomposition reaction of biomass pyrolysis, and their catalytic activity is limited to secondary reforming of bio-oil vapors. Wang et al. studied the catalytic effect of physically mixed K<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> on slow pyrolysis of pine wood in a packed bed reactor [100]. K<sub>2</sub>CO<sub>3</sub> lowered the decomposition of hemicellulose and cellulose, reduced liquid yields, and increased the yields of gaseous and char products, while Ca(OH)<sub>2</sub> completely removed the acids and aldehydes from the bio-oil with a significant increase in yield of alcohols without affecting the yields of pyrolysis products very much. Calcium cation has a weaker ionic strength than potassium cation, and it is generally expectable that calcium has a less catalytic activity on the biomass pyrolysis than potassium. Imran et al. used physically mixed Na<sub>2</sub>CO<sub>3</sub> for in-situ catalytic flash pyrolysis of jatropha seed cake in a bench scale entrained flow reactor setup [101]. Pyrolysis oil had spontaneous separation of aqueous phase and organic phase (bio-oil). The undesired compounds, acids and aldehydes were completely removed in the bio-oil and there was dramatic increase in the aliphatic and aromatic HCs. The bio-oil had very low oxygen content (7.1 wt.%), water content as low as 6.8 wt.%, a neutral pH, and a high calorific value upto 36.7 MJ/kg. These considerable improvement in the bio-oil were attributed to combined effect of Na<sub>2</sub>CO<sub>3</sub> and triglycerides content of jatropha cake.

In spite of the research works conducted on the effect of alkali metals on biomass primary decomposition, there is still a lack of systematic studies on the effect of alkali metals on the characteristics and chemical composition of the upgraded bio-oil. A summary of the catalytic effect of alkaline compounds on yields of biomass pyrolysis products and on bio-oil composition is presented in **Table 7**. In conclusion, alkali metals are capable of reducing undesired compounds of bio-oil particularly acids and enhancing the formation of some types of phenols which are regarded as high value products. Moreover, alkali metals could have a clear effect on lowering the biomass thermal degradation temperature.

**Table 7:** Summary of catalytic effect of alkaline compounds on yields of biomass pyrolysis products yields and bio-oil composition

Catalyst	Feed	Impregnation Method	Reactor type	Bio-Oil	Water	Gas	Char	HCs	CANs	FURs	PHEs	ALCs	ACIDs	ALDs	Ref.
<b>K<sub>2</sub>CO<sub>3</sub></b>	Pine wood	Physically mixed	Packed-bed reactor	-		+	+	+		-	+	-	-	-	[100]
<b>NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, and NaCl</b>	Wood	Wet impregnation	Packed-bed reactor	-	+	+	+		+	-	+				[93, 95, 102]
<b>KOH</b>	Fir wood	Wet impregnation	Packed-bed reactor	-	+	+	+		+		+				[97]
<b>Na<sub>2</sub>CO<sub>3</sub></b>	Jatropha seed cake	Physically mixed	Entrained flow reactor	-	+	+	+	+		-	-	-	-	-	[101]
<b>MgO</b>	Cotton seed	N/A	Tubular Packed Bed reactor	-		+	+	+							[103]
<b>CaO</b>	Pine wood	N/A	Fluidized-bed reactor	-	+	-	+			+	+		-		[104]
<b>Ca(OH)<sub>2</sub></b>	Pine wood	Physically mixed	Packed Bed reactor	+		-	+					+	-	-	[100]
<b>CaO</b>	Wood	N/A	Py/GC-MS					+		-	-	+	-	n/e	[105]

*+ and – signs indicate the increase and decrease in yield respectively, n/e indicates no or minimum effect, and blank column indicates the results are not reported (HCs-Hydrocarbons, CANs-Carbonyls, FURs- Furans, PHEs-Phenols, ALCs-Alcohols, ALDs-Aldehydes)*

### 2.3.2 Alkaline earth metal-based catalysts for catalytic pyrolysis of biomass

Alkaline earth metals have been extensively studied for tar cracking catalyst in gasification and the use of these base materials could be extended for upgrading of biomass pyrolysis oils. Alkaline earth metals are found in form of minerals and can be applied directly for catalysis without chemical treatment. The advantages of these materials are that they are abundant and are inexpensive compared to synthetic catalysts. The uncalcined forms of these materials are called limestone ( $\text{CaCO}_3$ ), magnesium carbonate ( $\text{MgCO}_3$ ), and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), respectively. These materials show high catalytic activity for tar elimination when calcined, calcination is a process where bound carbon dioxide is released upon heating. Calcined forms include calcites, magnesites, and calcined dolomites. Taralas et al. studied the catalytic pyrolysis of toluene with Norwegian dolomitic magnesium oxide [ $\text{MgO}$ ], Swedish low surface quicklime [ $\text{CaO}$ ], and calcined dolomite [ $\text{CaMg}(\text{O})_2$ ] and found the performance of all mineral catalysts superior to metal modified alumina ( $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ ) and the catalytic effect followed the sequence:  $\text{CaO} > \text{CaMg}(\text{O})_2 > \text{MgO} > \text{alumina}$  [106].

Calcined limestone could be potential catalyst for catalytic upgrading of bio-oil. catalytic pyrolysis of mahua seed [107] and Karanja tree [108] with  $\text{CaO}$  was investigated by Shadangi and Mohanty et al. leading to the production of a bio-oil with high pH, viscosity, and heating value. Ding et al. reported that  $\text{CaO}$  could increase catalytic decarboxylation by conversion of acid compounds to hydrocarbons. [109]. Lu et al. used various metal oxides for reforming of poplar wood pyrolysis vapors in a Py-GC/MS [105]. They claimed that  $\text{CaO}$  removed the acids, reduced the heavy products like anhydrosugars, while it increased the formation of desired compounds such as cyclopentanones, hydrocarbons, and several light compounds like acetaldehyde, acetone, 2- butanone, and methanol. Lin et al. used  $\text{CaO}$  to study the effect of catalyst-to-biomass ratios for *in-situ* deoxygenation of pine wood pyrolysis vapors in a fluidized-bed reactor [104]. They found that high catalyst-to-biomass ratios lowered the oxygen content of bio-oil while water content of the bio-oil was almost doubled. Moreover,  $\text{CaO}$  reduced the gas yields from 19% to 10% and this reduction was attributed to the absorption of  $\text{CO}_2$  on  $\text{CaO}$  forming  $\text{CaCO}_3$ . While dramatic decreases were observed in the yield of some liquid phase compounds including laevoglucose, D-allose, and acidic compounds.

Pütün et al. applied  $\text{MgO}$  for catalytic pyrolysis of cotton seed in a tubular packed bed and found decreases in oil yields whereas increases in gas and char yields were recorded [103]. However, the quality of bio-oil was improved in terms of calorific value, hydrocarbon distribution, and removal of oxygenated groups. In addition to that, they also stated that  $\text{MgO}$  removed up to 50% of oxygen, converted long chain alkanes and alkenes to lower molecular weight hydrocarbons, and increased the aliphatic and aromatic fractions of the bio-oil. Stefanidis et al. compared the performance of  $\text{MgO}$  and ZSM-5 for catalytic pyrolysis of beech wood sawdust in a bench-scale fixed bed tubular reactor [110]. Accordingly,  $\text{MgO}$  effectively decreased the oxygen content of the bio- oil and exhibited similar or even better performance compared to that of ZSM-5. Analyzing product distribution and the composition of the bio-oil revealed that the basic sites of the  $\text{MgO}$  favored the reduction of acids and deoxygenation via ketonization and aldol condensation reactions, removing oxygen mainly as  $\text{CO}_2$ .  $\text{MgO}$  also exhibited better regeneration characteristics upon coke combustion compared to that of ZSM-5. Zhang et al. reported

significant increases in the yield of aromatics in bio-oil, when studied the synergistic effect of the addition of MgO, CaO, spent FCC, and ZSM-5 during the pyrolysis of pine sawdust in a Py-GC/MS [111]. The addition of these base catalysts led to efficient cracking of high-oxygenated compounds into low oxygenated compounds and with the subsequent conversion of the low oxygenated compounds into aromatics. Dolomites are considered the most popular and cheap catalyst for tar elimination and calcined dolomite has shown high efficiency for removing tar from the product gases of gasifier. Veses et al. applied dolomite and CaO for in-situ upgrading of wood pyrolysis in an auger reactor and recorded remarkable decreases in oxygen content and acidity of the bio-oil and the resulted bio-oil had a higher pH and calorific values. [112].

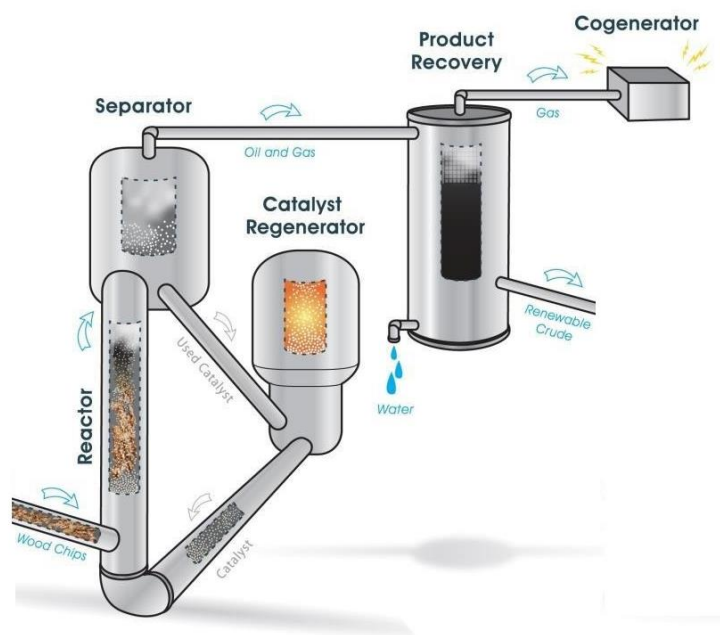
Overall, research on the effect of alkaline earth metal-based catalysts on biomass pyrolysis is very limited and a lot more needs to be done to evaluate their potentials for biomass pyrolysis in general and for biofuels production in particular. Nevertheless, the preliminary studies have shown their potential for deoxygenation of bio-oil and positive indication to produce more desirable compounds in bio-oil such as alkanes and aromatics with suppressed formation of undesirable compounds such as acids. In general, alkaline earth metals lead to decreased bio-oil yields and increased water and char yields. It should be noted that the main interest in application of these mineral compounds in biomass catalytic pyrolysis lies in their abundance in nature and being inexpensive, favoring the economic aspects of biofuels production.

## 2.4 Catalytic pyrolysis of biomass at pilot and demonstration scales

Recently, a few activities have been initiated to implement catalytic fast pyrolysis at industrial demonstration scale. KiOR Inc. announced their start-up production unit in Mississippi using their biomass fluidized catalytic cracking (BFCC) process with a capacity of 500 ton/d biomass, yielding 67 gallon bio- oil/ton of biomass [113]. The BFCC process schematic is presented in **Figure 5**, It is infect a FCC-type process where catalyst is employed replacing a proportion of the heating media (sand) in a fluidized bed reactor and the coked catalyst is regenerated in a combustor. There is not much information available on the catalyst type and product quality but KiOR claimed to produce gasoline and diesel blend stocks using their catalyst through the BFCC process. Moreover, they argue that the products are comparable to their fossil-oriented counterparts. RTI International (Research Triangle Institute) has also developed such a catalytic biomass pyrolysis process with 1 ton/d biomass capacity. The pilot plant is based on a single-loop transport reactor design with continuous catalyst circulation and regeneration [114] and has been successfully operated with a novel catalyst producing a bio-crude intermediate with 24 wt.% oxygen.

Another successful example is the novel cyclonic reactor system “PyRos” which was adopted for online *in-situ* catalytic pyrolysis of biomass [115]. Cyclonic reactor provides the substantial advantage of a very short vapor residence time (less than half a second) over existing pyrolysis technologies, e.g., fluidized bed reactor systems, and can considerably improve the liquid yields and properties by avoiding excessive secondary cracking and contact of vapors with coke and char. The schematic presentation of the

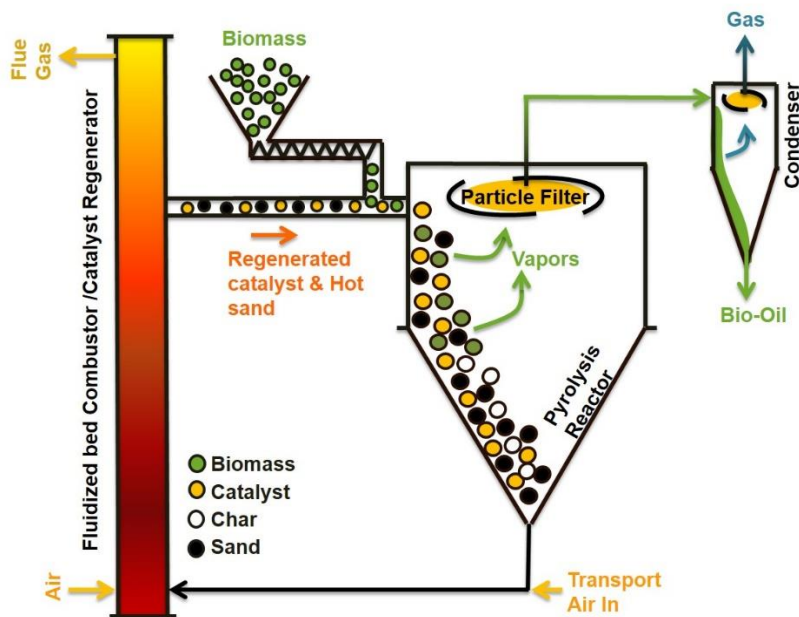
process is depicted in **Figure 6**. It is also a FCC-type process that could provide a suitable solution for continuous production of bio-fuel and regeneration of coked catalyst. PyRos has also introduced a novel sodium-based alumina catalyst whose product characteristics have been reported based on a lab scale testing unit [52]. The preliminary findings showed that this catalyst could be implemented in the current pilot scale pyrolysis technologies and could be scaled up for commercial production of biofuels. A reactor concept with a mobile catalyst phase and an integrated catalyst regeneration unit seems to be a promising option for the scale up of this technology. A conceptual process flow sheet for the production of green fuels via catalytic fast pyrolysis is presented in the graphical abstract of this article that may be integrated with the existing refinery structure.



**Figure 5:** KiOR BFCC process [113]

Apparently, catalyst development is key for the success of commercial production of biofuels and a breakthrough in catalyst development could be instrumental. Based on the present review, zeolites could be considered as the most extensively studied catalysts for catalytic biomass pyrolysis and hold the highest potential to tailor the bio-oil properties for biofuels application. The main problems that need to overcome with zeolites are, to avoid deep cracking and formation of gas which reduces liquid yields, to avoid deep deoxygenation that yields a polyaromatic product, and to avoid severe catalyst deactivation due to coke formation. Deep cracking and formation of gas may be controlled by manipulating the strength and concentration of acid sites in zeolites. Formation of polyaromatics may not be avoided as it arises from the low hydrogen content of biomass. From this point of view, a selective deoxygenation, which leaves behind part of the oxygen in the bio-oil may be a more attractive option. Only, the resulting mixture should be made suitable for blending with hydrocarbon fuels for further processing. Formation of coke and catalyst deactivation is not a major problem in an FCC-type pyrolysis operation, where combustion of coke deposited on the catalyst generates the energy required to run the

endothermic cracking process. Up to date, research on catalytic pyrolysis of biomass has shown promising results but further studies are required to design a more dedicated catalyst to carry out selective deoxygenation of the bio-oil and to maximize yield of diesel and gasoline range hydrocarbons.



**Figure 6:** PyRos Reactor System [115]

## 2.5 Conclusions

Zeolites are capable of reducing the concentration of oxygenated compounds present in biomass pyrolysis liquid via deoxygenation reactions (such as dehydration, decarbonylation, and decarboxylation), while increasing the concentration of hydrocarbon and aromatic species. Another advantage of zeolites is decreased molecular weight of the bio-oil through cracking lignin-derived compounds. Nevertheless, there are also drawbacks associated with the application of relatively small pore sized zeolites including significant decreases in the yield of the organic phase of bio-oil caused by increased production of water and gas as well as by rapid catalyst deactivation through coke deposition. Compared to zeolites, larger pore sized aluminosilicates are less susceptible to catalyst deactivation and therefore, relatively higher organic yields could be expected. However, it should be noted that the performance of the aluminosilicates has not always been found superior to that of the conventional zeolites. In general, these mesoporous catalysts have been revealed to possess less activity compared to ZSM-5 under the same conditions. Overall and as a key point, a careful tuning of the pore size and acidity of these catalysts could improve their product selectivity.

Studies on the effects of alkaline compounds addition on the pyrolysis of lignocellulosic materials are not extensive and their catalytic effects on the characteristics of biomass pyrolysis products are yet to be systematically investigated. A detailed analysis of bio-oil

characteristics is also lacking. Such information would be needed to evaluate the potentials of alkaline compounds for their implementation as catalyst for biofuels production. Nevertheless, some of their qualitative features are well evident revealing that alkali metals could result in increases in yields of char, gas, and water as well as reductions in organic liquid contents owing to enhancements in dehydration, decarboxylation, and charring reactions. Moreover, alkali metals are also effective on converting higher molecular weight compounds such as levoglucosan into lower molecular weight compounds formation. Finally, the preliminary findings have revealed the potentials of alkaline earth metals for deoxygenation of bio-oil, production of hydrocarbons, and reduction of undesired compounds in particular acids. Nevertheless, further systemic studies would be required to explore their full catalytic potential for production of biofuels.



## 2.7 References

1. Sadeghbeigi, R., *CHAPTER 3 - FCC Catalysts*, in *Fluid Catalytic Cracking Handbook (Second Edition)*, R. Sadeghbeigi, Editor. 2000, Gulf Professional Publishing: Houston. p. 84-124.
2. Bhatia, S., *Zeolite catalysts: principles and applications*. 1989: CRC press.
3. Kirk-Othmer, *Encyclopedia of Chemical Technology*. 2007.
4. Horne, P.A. and P.T. Williams, *Climate change Energy and the environment Premium quality fuels and chemicals from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. *Renewable Energy*, 1994. **5**(5): p. 810-812.
5. Williams, P.T. and P.A. Horne, *Characterisation of oils from the fluidised bed pyrolysis of biomass with zeolite catalyst upgrading*. *Biomass and Bioenergy*, 1994. **7**(1-6): p. 223-236.
6. Horne, P.A., N. Nugranad, and P.T. Williams, *Catalytic coprocessing of biomass-derived pyrolysis vapours and methanol*. *Journal of Analytical and Applied Pyrolysis*, 1995. **34**(1): p. 87-108.
7. Williams, P.T. and P.A. Horne, *Analysis of aromatic hydrocarbons in pyrolytic oil derived from biomass*. *Journal of Analytical and Applied Pyrolysis*, 1995. **31**: p. 15-37.
8. Horne, P.A. and P.T. Williams, *Upgrading of biomass-derived pyrolytic vapours over zeolite ZSM-5 catalyst: effect of catalyst dilution on product yields*. *Fuel*, 1996. **75**(9): p. 1043-1050.
9. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. *Energy & Fuels*, 2000. **14**(6): p. 1161-1167.
10. Williams, P.T. and N. Nugranad, *Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks*. *Energy*, 2000. **25**(6): p. 493-513.
11. Wojciechowski, B.W. and A. Corma, *Catalytic cracking: Catalysts, chemistry, and kinetics*. 1986. Medium: X; Size: Pages: 248.
12. Gayubo, A.G., et al., *Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. I. Alcohols and Phenols*. *Industrial & Engineering Chemistry Research*, 2004. **43**(11): p. 2610-2618.
13. Hoff, T.C., et al., *Tailoring ZSM-5 Zeolites for the Fast Pyrolysis of Biomass to Aromatic Hydrocarbons*. *ChemSusChem*, 2016. **9**(12): p. 1473-1482.
14. Le, H.D., et al., *Reactions of Model Compounds of Biomass-Pyrolysis Oils over ZSM-5 Zeolite Catalysts, in Pyrolysis Oils from Biomass*. 1988, American Chemical Society. p. 328-341.
15. Chang, C.C. and L.L. Hegedus, *Surface reactions of NO, CO, and O<sub>2</sub> near the stoichiometric point*. *Journal of Catalysis*, 1979. **57**(3): p. 361-371.
16. Gayubo, A.G., et al., *Transformation of Oxygenate Components of Biomass Pyrolysis Oil on a HZSM-5 Zeolite. II. Aldehydes, Ketones, and Acids*. *Industrial & Engineering Chemistry Research*, 2004. **43**(11): p. 2619-2626.
17. Gayubo, A.G., et al., *Undesired components in the transformation of biomass pyrolysis oil into hydrocarbons on an HZSM-5 zeolite catalyst*. *Journal of Chemical Technology & Biotechnology*, 2005. **80**(11): p. 1244-1251.



18. Carlson, T.R., T.P. Vispute, and G.W. Huber, *Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds*. ChemSusChem, 2008. **1**(5): p. 397-400.
19. Carlson, T., et al., *Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks*. Topics in Catalysis, 2009. **52**(3): p. 241-252.
20. Simell, P.A., J.K. Leppälähti, and J.B.s. Bredenberg, *Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials*. Fuel, 1992. **71**(2): p. 211-218.
21. French, R. and S. Czernik, *Catalytic pyrolysis of biomass for biofuels production*. Fuel Processing Technology, 2010. **91**(1): p. 25-32.
22. Karnjanakom, S., et al., *Selectively catalytic upgrading of bio-oil to aromatic hydrocarbons over Zn, Ce or Ni-doped mesoporous rod-like alumina catalysts*. Journal of Molecular Catalysis A: Chemical, 2016. **421**: p. 235-244.
23. Thangalazhy-Gopakumar, S., et al., *Catalytic pyrolysis of green algae for hydrocarbon production using H+ZSM-5 catalyst*. Bioresource Technology, 2012. **118**: p. 150-157.
24. Lisa, K., A.R. Stanton, and S. Czernik, *Production of Hydrocarbon Fuels from Biomass by Catalytic Fast Pyrolysis*. 2012.
25. Li, J., et al., *Catalytic fast pyrolysis of biomass with mesoporous ZSM-5 zeolites prepared by desilication with NaOH solutions*. Applied Catalysis A: General, 2014. **470**: p. 115-122.
26. Mullen, C.A. and A.A. Boateng, *Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites*. ACS Sustainable Chemistry & Engineering, 2015. **3**(7): p. 1623-1631.
27. Fischer, A., et al., *The effect of temperature, heating rate, and ZSM-5 catalyst on the product selectivity of the fast pyrolysis of spent coffee grounds*. RSC Advances, 2015. **5**(37): p. 29252-29261.
28. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts*. Journal of Analytical and Applied Pyrolysis, 2008. **81**(1): p. 72-79.
29. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Evaluation of catalytic pyrolysis of cassava rhizome by principal component analysis*. Fuel, 2010. **89**(1): p. 244-253.
30. Engtrakul, C., et al., *Effect of ZSM-5 acidity on aromatic product selectivity during upgrading of pine pyrolysis vapors*. Catalysis Today, 2016. **269**: p. 175-181.
31. Sun, L., et al., *Comparison of catalytic fast pyrolysis of biomass to aromatic hydrocarbons over ZSM-5 and Fe/ZSM-5 catalysts*. Journal of Analytical and Applied Pyrolysis, 2016. **121**: p. 342-346.
32. Liang, J., et al., *Enhancement of bio-oil yield and selectivity and kinetic study of catalytic pyrolysis of rice straw over transition metal modified ZSM-5 catalyst*. Journal of Analytical and Applied Pyrolysis, 2017. **128**: p. 324-334.
33. Xiang, Z., et al., *Thermal behavior and kinetic study for co-pyrolysis of lignocellulosic biomass with polyethylene over Cobalt modified ZSM-5 catalyst by thermogravimetric analysis*. Bioresource Technology, 2018. **247**: p. 804-811.
34. Nguyen, T.S., et al., *Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts*. Bioresource Technology, 2013. **142**(0): p. 353-360.
35. Aho, A., et al., *Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure*. Fuel, 2008. **87**(12): p. 2493-2501.

36. Jae, J., et al., *Catalytic fast pyrolysis of lignocellulosic biomass in a process development unit with continual catalyst addition and removal*. Chemical Engineering Science, 2014. **108**: p. 33-46.
37. Yildiz, G., et al., *Catalytic Fast Pyrolysis of Pine Wood: Effect of Successive Catalyst Regeneration*. Energy & Fuels, 2014. **28**(7): p. 4560-4572.
38. Yildiz, G., et al., *In situ performance of various metal doped catalysts in micro-pyrolysis and continuous fast pyrolysis*. Fuel Processing Technology, 2016. **144**: p. 312-322.
39. Paasikallio, V., et al., *Catalytic Pyrolysis of Forest Thinnings with ZSM-5 Catalysts: Effect of Reaction Temperature on Bio-oil Physical Properties and Chemical Composition*. Energy & Fuels, 2013. **27**(12): p. 7587-7601.
40. Mante, O.D., et al., *Catalytic pyrolysis with ZSM-5 based additive as co-catalyst to Y-zeolite in two reactor configurations*. Fuel, 2014. **117, Part A**: p. 649-659.
41. Lappas, A.A., et al., *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
42. Bertero, M. and U. Sedran, *Immediate catalytic upgrading of soybean shell bio-oil*. Energy, 2016. **94**: p. 171-179.
43. Iliopoulou, E.F., et al., *Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours*. Green Chemistry, 2014. **16**(2): p. 662-674.
44. Iliopoulou, E.F., et al., *Catalytic upgrading of biomass pyrolysis vapors using transition metal-modified ZSM-5 zeolite*. Applied Catalysis B: Environmental, 2012. **127**: p. 281-290.
45. Feroso, J., et al., *Lamellar and pillared ZSM-5 zeolites modified with MgO and ZnO for catalytic fast-pyrolysis of eucalyptus woodchips*. Catalysis Today, 2016. **277**: p. 171-181.
46. Hernando, H., et al., *Biomass catalytic fast pyrolysis over hierarchical ZSM-5 and Beta zeolites modified with Mg and Zn oxides*. Biomass Conversion and Biorefinery, 2017. **7**(3): p. 289-304.
47. Olazar, M., et al., *Pyrolysis of sawdust in a conical spouted-bed reactor with a HZSM-5 catalyst*. AIChE Journal, 2000. **46**(5): p. 1025-1033.
48. Atutxa, A., et al., *Kinetic Description of the Catalytic Pyrolysis of Biomass in a Conical Spouted Bed Reactor*. Energy & Fuels, 2005. **19**(3): p. 765-774.
49. Zhang, H., et al., *Catalytic fast pyrolysis of biomass in a fluidized bed with fresh and spent fluidized catalytic cracking (FCC) catalysts*. Energy & Fuels, 2009. **23**(12): p. 6199-6206.
50. Zhang, H., et al., *Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor*. Bioresource Technology, 2009. **100**(3): p. 1428-1434.
51. Antonakou, E.V., V.S. Dimitropoulos, and A.A. Lappas, *Production and characterization of bio-oil from catalytic biomass pyrolysis*. Thermal Science, 2006. **10**(3): p. 151-160.
52. Imran, A., et al., *High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate*. Fuel Processing Technology, 2014. **127**(0): p. 72-79.

53. Pütün, E., B.a.B. Uzun, and A.e.E. Pütün, *Rapid pyrolysis of olive residue. 2. Effect of catalytic upgrading of pyrolysis vapors in a two-stage fixed-bed reactor*. Energy & Fuels, 2009. **23**(4): p. 2248-2258.
54. Williams, P.T. and P.A. Horne, *The influence of catalyst type on the composition of upgraded biomass pyrolysis oils*. Journal of Analytical and Applied Pyrolysis, 1995. **31**: p. 39-61.
55. Horne, P.A. and P.T. Williams, *The effect of zeolite ZSM-5 catalyst deactivation during the upgrading of biomass-derived pyrolysis vapours*. Journal of Analytical and Applied Pyrolysis, 1995. **34**(1): p. 65-85.
56. Stephanidis, S., et al., *Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: Effect of hydrothermal pre-treatment of biomass*. Catalysis Today, 2011. **167**(1): p. 37-45.
57. Li, P., et al., *Effects of Fe-, Zr-, and Co-Modified Zeolites and Pretreatments on Catalytic Upgrading of Biomass Fast Pyrolysis Vapors*. Energy & Fuels, 2016. **30**(4): p. 3004-3013.
58. Li, B., et al., *Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed*. Fuel, 2014. **129**: p. 61-67.
59. Antonakou, E., et al., *Evaluation of various types of Al-MCM-41 materials as catalysts in biomass pyrolysis for the production of bio-fuels and chemicals*. Fuel, 2006. **85**(14–15): p. 2202-2212.
60. Beck, J.S., et al., *A new family of mesoporous molecular sieves prepared with liquid crystal templates*. Journal of the American Chemical Society, 1992. **114**(27): p. 10834-10843.
61. Bridgwater, A.V., *Principles and practice of biomass fast pyrolysis processes for liquids*. Journal of Analytical and Applied Pyrolysis, 1999. **51**(1–2): p. 3-22.
62. Noreña-Franco, L., et al., *Selective hydroxylation of phenol employing Cu-MCM-41 catalysts*. Catalysis Today, 2002. **75**(1–4): p. 189-195.
63. Savidha, R., et al., *A comparative study on the catalytic activity of Zn and Fe containing Al-MCM-41 molecular sieves on t-butylation of phenol*. Journal of Molecular Catalysis A: Chemical, 2004. **211**(1–2): p. 165-177.
64. Carvalho, W.A., M. Wallau, and U. Schuchardt, *Iron and copper immobilised on mesoporous MCM-41 molecular sieves as catalysts for the oxidation of cyclohexane*. Journal of Molecular Catalysis A: Chemical, 1999. **144**(1): p. 91-99.
65. Chaudhari, K., et al., *Mesoporous Aluminosilicate of the MCM-41 Type: Its Catalytic Activity in n-Hexane Isomerization*. Journal of Catalysis, 1999. **186**(1): p. 81-90.
66. Parvulescu, V. and B.L. Su, *Iron, cobalt or nickel substituted MCM-41 molecular sieves for oxidation of hydrocarbons*. Catalysis Today, 2001. **69**(1–4): p. 315-322.
67. Nesterenko, N.S., et al., *Dehydrogenation of ethylbenzene and isobutane over Ga- and Fe-containing mesoporous silicas*. Applied Catalysis A: General, 2003. **254**(2): p. 261-272.
68. Corma, A., A. Martínez, and V. Martínez-Soria, *Hydrogenation of Aromatics in Diesel Fuels on Pt/MCM-41 Catalysts*. Journal of Catalysis, 1997. **169**(2): p. 480-489.

69. Albertazzi, S., et al., *Hydrogenation and hydrogenolysis/ring-opening of naphthalene on Pd/Pt supported on zirconium-doped mesoporous silica catalysts*. Journal of Catalysis, 2004. **228**(1): p. 218-224.
70. Lewandowska, A., et al., *MCM-41 mesoporous molecular sieves supported nickel—physico-chemical properties and catalytic activity in hydrogenation of benzene*. Journal of Molecular Catalysis A: Chemical, 2002. **188**(1–2): p. 85-95.
71. He, N.-Y., S.-L. Bao, and Q.-H. Xu, *Synthesis and characterization of FeSiMCM-41 and LaSiMCM-41*, in *Studies in Surface Science and Catalysis*, S.-K.I. Hakze Chon and U. Young Sun, Editors. 1997, Elsevier. p. 85-92.
72. Corma, A., M.T. Navarro, and J.P.r. Pariente, *Synthesis of an ultralarge pore titanium silicate isomorphous to MCM-41 and its application as a catalyst for selective oxidation of hydrocarbons*. Journal of the Chemical Society, Chemical Communications, 1994(2): p. 147-148.
73. Corma, A., et al., *Preparation and properties of Ti-containing MCM-41*, in *Studies in Surface Science and Catalysis*, H.G.K.H.P. J. Weitkamp and W. Hölderich, Editors. 1994, Elsevier. p. 69-75.
74. Luan, Z., et al., *Synthesis and spectroscopic characterization of vanadosilicate mesoporous MCM-41 molecular sieves*. The Journal of Physical Chemistry, 1996. **100**(50): p. 19595-19602.
75. Wu, Q., et al., *Copper/MCM-41 as catalyst for the wet oxidation of phenol*. Applied Catalysis B: Environmental, 2001. **32**(3): p. 151-156.
76. Corma, A., *Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions*. Chemical Reviews, 1995. **95**(3): p. 559-614.
77. Occelli, M.L., S. Biz, and A. Auroux, *Effects of isomorphous substitution of Si with Ti and Zr in mesoporous silicates with the MCM-41 structure*. Applied Catalysis A: General, 1999. **183**(2): p. 231-239.
78. Takeguchi, T., et al., *Synthesis and Characterization of Alkali-free, Ga-Substituted MCM-41 and Its Performance for n-Hexane Conversion*. Journal of Catalysis, 1998. **175**(1): p. 1-6.
79. Pârvulescu, V., C. Anastasescu, and B.L. Su, *Bimetallic Ru-(Cr, Ni, or Cu) and La-(Co or Mn) incorporated MCM-41 molecular sieves as catalysts for oxidation of aromatic hydrocarbons*. Journal of Molecular Catalysis A: Chemical, 2004. **211**(1–2): p. 143-148.
80. Adam, J., et al., *In situ catalytic upgrading of biomass derived fast pyrolysis vapours in a fixed bed reactor using mesoporous materials*. Microporous and Mesoporous Materials, 2006. **96**(1–3): p. 93-101.
81. Adam, J., et al., *Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts*. Fuel, 2005. **84**(12–13): p. 1494-1502.
82. Ciesla, U. and F. Schüth, *Ordered mesoporous materials*. Microporous and Mesoporous Materials, 1999. **27**(2–3): p. 131-149.
83. Twaiq, F.A., A.R. Mohamed, and S. Bhatia, *Liquid hydrocarbon fuels from palm oil by catalytic cracking over aluminosilicate mesoporous catalysts with various Si/Al ratios*. Microporous and Mesoporous Materials, 2003. **64**(1–3): p. 95-107.
84. Iliopoulou, E.F., et al., *Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts*. Chemical Engineering Journal, 2007. **134**(1–3): p. 51-57.



85. Saijonkari-Pahkala, K., *Non-wood plants as raw material for pulp and paper*. Vol. 10. 2001, Finland.
86. Czernik, S. and A.V. Bridgwater, *Overview of Applications of Biomass Fast Pyrolysis Oil*. *Energy & Fuels*, 2004. **18**(2): p. 590-598.
87. Bradbury, A.G.W., Y. Sakai, and F. Shafizadeh, *A kinetic model for pyrolysis of cellulose*. *Journal of Applied Polymer Science*, 1979. **23**(11): p. 3271-3280.
88. White, J.E., W.J. Catallo, and B.L. Legendre, *Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural residue case studies*. *Journal of Analytical and Applied Pyrolysis*, 2011. **91**(1): p. 1-33.
89. Raveendran, K., A. Ganesh, and K.C. Khilar, *Influence of mineral matter on biomass pyrolysis characteristics*. *Fuel*, 1995. **74**(12): p. 1812-1822.
90. Liden, A., F. Berruti, and D. Scott, *A kinetic model for the production of liquids from the flash pyrolysis of biomass*. *Chemical Engineering Communications*, 1988. **65**(1): p. 207-221.
91. Jahirul, M., et al., *Biofuels Production through Biomass Pyrolysis — A Technological Review*. *Energies*, 2012. **5**(12): p. 4952.
92. Fahmi, R., et al., *The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow*. *Fuel*, 2007. **86**(10–11): p. 1560-1569.
93. Di Blasi, C., A. Galgano, and C. Branca, *Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis*. *Industrial & Engineering Chemistry Research*, 2009. **48**(7): p. 3359-3369.
94. Di Blasi, C., C. Branca, and A. Galgano, *Effects of Diammonium Phosphate on the Yields and Composition of Products from Wood Pyrolysis*. *Industrial & Engineering Chemistry Research*, 2006. **46**(2): p. 430-438.
95. Di Blasi, C., C. Branca, and A. Galgano, *Thermal and catalytic decomposition of wood impregnated with sulfur- and phosphorus-containing ammonium salts*. *Polymer Degradation and Stability*, 2008. **93**(2): p. 335-346.
96. Wang, J., et al., *Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass*. *Thermochimica Acta*, 2006. **444**(1): p. 110-114.
97. Di Blasi, C., A. Galgano, and C. Branca, *Effects of Potassium Hydroxide Impregnation on Wood Pyrolysis*. *Energy & Fuels*, 2009. **23**(2): p. 1045-1054.
98. Jensen, A., et al., *TG-FTIR Study of the Influence of Potassium Chloride on Wheat Straw Pyrolysis*. *Energy & Fuels*, 1998. **12**(5): p. 929-938.
99. Nowakowski, D.J., et al., *Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice*. *Fuel*, 2007. **86**(15): p. 2389-2402.
100. Wang, Z., et al., *Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst*. *Fuel Processing Technology*, 2010. **91**(8): p. 942-950.
101. Imran, A., et al., *Catalytic flash pyrolysis of oil-impregnated-wood and jatropha cake using sodium based catalysts*. *Journal of Analytical and Applied Pyrolysis*, 2016. **117**: p. 236-246.
102. Di Blasi, C., C. Branca, and A. Galgano, *Effects of Diammonium Phosphate on the Yields and Composition of Products from Wood Pyrolysis*. *Industrial & Engineering Chemistry Research*, 2007. **46**(2): p. 430-438.
103. Pütün, E., *Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst*. *Energy*, 2010. **35**(7): p. 2761-2766.

104. Lin, Y., et al., *Deoxygenation of Bio-oil during Pyrolysis of Biomass in the Presence of CaO in a Fluidized-Bed Reactor*. Energy & Fuels, 2010. **24**(10): p. 5686-5695.
105. Lu, Q., et al., *Catalytic Upgrading of Biomass Fast Pyrolysis Vapors with Nano Metal Oxides: An Analytical Py-GC/MS Study*. Energies, 2010. **3**(11): p. 1805.
106. Taralas, G. and M.G. Kontominas, *Kinetic modelling of VOC catalytic steam pyrolysis for tar abatement phenomena in gasification/pyrolysis technologies*. Fuel, 2004. **83**(9): p. 1235-1245.
107. Shadangi, K.P. and K. Mohanty, *Comparison of yield and fuel properties of thermal and catalytic Mahua seed pyrolytic oil*. Fuel, 2014. **117**: p. 372-380.
108. Shadangi, K.P. and K. Mohanty, *Thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel*. Fuel, 2014. **115**: p. 434-442.
109. Ding, L., et al., *Naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts*. Applied Catalysis A: General, 2009. **371**(1–2): p. 121-130.
110. Stefanidis, S.D., et al., *Natural magnesium oxide (MgO) catalysts: A cost-effective sustainable alternative to acid zeolites for the in situ upgrading of biomass fast pyrolysis oil*. Applied Catalysis B: Environmental, 2016. **196**: p. 155-173.
111. Zhang, H., et al., *Study on Pyrolysis of Pine Sawdust with Solid Base and Acid Mixed Catalysts by Thermogravimetry–Fourier Transform Infrared Spectroscopy and Pyrolysis–Gas Chromatography/Mass Spectrometry*. Energy & Fuels, 2014. **28**(7): p. 4294-4299.
112. Veses, A., et al., *Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts*. Bioresource Technology, 2014. **162**: p. 250-258.
113. KiOR, I. *KiOR Production Facilities*. 2016; Available from: <http://www.kior.com/>.
114. Dayton, D.C., et al., *Design and operation of a pilot-scale catalytic biomass pyrolysis unit*. Green Chemistry, 2015. **17**(9): p. 4680-4689.
115. Brem, G. and E.A. Bramer. *PyRos: a new flash pyrolysis technology for the production of bio-oil from biomass residues*. in *International Conference & Exhibition Bioenergy Outlook*. 2007. Singapore.

## CHAPTER 3:

# Catalytic flash pyrolysis of biomass using different types of zeolite and online vapor fractionation<sup>2</sup>

**ABSTRACT:** Bio-oil produced from conventional flash pyrolysis has a poor quality and needs an expensive up-gradating before it can be used as a transportation fuel. In this work, a high-quality bio-oil has been produced using a novel approach where flash pyrolysis, catalysis and fractionation of pyrolysis vapors using two stage condensation are combined in a single process unit. A bench scale unit of 1 kg/h feedstock capacity is used for catalytic pyrolysis in an entrained down-flow reactor system equipped with two staged condensation of pyrolysis vapor. Zeolites based catalysts are investigated to study the effect of varying acidities of Faujasite Y zeolites, zeolite structures (ZSM5), different catalyst to biomass ratios and the different catalytic pyrolysis temperatures. Low catalyst/biomass ratios did not show any significant improvements in the quality of bio-oil, while high catalyst/biomass ratios showed an effective deoxygenation of the bio-oil. The application of zeolites decreased the organic liquid yield due to the increase of the production of non-condensables, primarily hydrocarbons. The catalytically produced bio-oil was less viscous and zeolites were effective to crack heavy molecular weight compounds in the bio-oil. Acidic zeolites, H-Y and H-ZSM5, increased the desirable chemical compounds in the bio-oil such as phenols, furans and hydrocarbon, and reduced the undesired compounds such as acids. On the other hand reducing the acidity of zeolites reduced some of the undesired compounds in the bio-oil such as ketones and aldehydes. The H-Y performance was superior to the rest of zeolites studied: bio-oil of high chemical and calorific value was produced with a high organic liquid yield and low oxygen content. H-ZSM5 was a close competitor to H-Y in performance but with a lower yield of bio-oil. Online fractionation of catalytic pyrolysis vapors was employed by controlling the condensers temperature and proved to be a successful process parameter to tailor the desired properties of bio-oil. A high calorific value bio-oil having up to 90% organics was produced using two staged condensation of catalytic pyrolysis vapor. Zeolites based acidic catalysts can be used for selective de-oxygenation, the quality of catalytic bio-oil can be further improved with staged condensation of vapors.

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### 3.1 Introduction

There are a variety of techniques to produce energy and sustainable fuels from biomass, and recently the interest in producing the bio-oil via flash pyrolysis of biomass is increasing. However, the bio-oil obtained via conventional flash pyrolysis is very different from crude oil originating from petroleum sources. Compared to fossil oil, the bio-oil is rich in oxygen containing molecules, it has a heating value of about half of that of the conventional fuel oil and it is partly miscible with conventional fuels. Due to these properties many problems arise in the handling and utilization of the bio-oil [1]. Therefore, the bio-oil obtained from conventional flash pyrolysis needs to be upgraded before it can be used as a transportation fuel. For catalytic up-grading of bio-oil, a number of process routes have been explored using various catalysts. De-oxygenation of bio-oil can be carried out by a hydro-treating process with a zeolite based catalyst. This hydro-de-oxygenation (HDO) process is similar to the hydro-desulfurization (HDS) process i.e is an essential part of oil refining [2]. Hydro-treating requires large volumes of hydrogen which has a negative impact on the process economics. However, research on catalytic after-treatment of bio-oil has not shown any promising results. Catalytic after-treatment processes suffer from fast deactivation of the catalyst caused by coking and poor yield of hydrocarbons due to bypassing of the larger molecules in bio-oils [3].

The oxygen content of bio-oils is usually very high up to 45 wt. % [[3, 4]. The type of oxygen component depends on the raw material and on the conditions of the pyrolysis process (temperature, residence time and heating rate) [5-7]. In bio-oil, typically carboxyl, carbonyl, hydroxyl and methoxy functionalities are present [5, 7-9]. These oxygenate components are mainly responsible for most of the deleterious properties of the bio-oil such as high viscosity, non-volatility, high acidity and resulting corrosiveness and extreme instability upon storage, lower energy density than the conventional fuel by 50%, immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air [5-8, 10, 11]. Thus, upgrading of bio-oil means removal of oxygen. As bio-oil contains large molecules derived from lignin, the use of cracking catalysts could selectively break down the lignin derivatives in the bio-oil. Since the lignin derivatives also contain a high proportion of oxygen [12], breaking down these molecules will decrease the oxygen content and increase the hydrocarbons in the bio-oil, and with resulting high heating value of the bio-oil.

In order to improve bio-oil quality, several catalysts have been proposed in literature. In-situ catalytic flash pyrolysis of biomass over zeolite type catalysts has gained the interest in past decade because it does not require reducing gases, and the process release the oxygen as carbon dioxide and water. The catalytically produced bio-oil presents a series of improved properties, such as stability and lower acidity. Lappas et al. [13] have proposed that the bio-oil stability depends on the catalyst type and activity (in addition to pyrolysis process conditions). It is a challenge to develop a single catalyst that can selectively removes problematic oxygenates in bio-oil and till now most of studies have been based on off the shelf catalysts with little efforts to design dedicated catalysts that can tailor the targeted properties of bio-oil. In the present work, zeolites-based catalysts are being developed and optimised based on lab scale studies of biomass model components. The criteria for catalyst development is (i) de-oxygenation of oxygenate



components in the vapor phase in-situ during the pyrolysis process, (ii) acceleration of primary cracking and (iii) inhibition of secondary cracking. Zeolites are typical fluid catalytic cracking (FCC) catalysts being used in oil refining industry for upgrading low-octane components in the gasoline boiling range, and to isomerize low-octane linear olefins to high-octane branched olefins [14]. Zeolites have a low price and have rich experience to use in FCC units. The key properties of zeolites that influence their acidity, thermal stability, and overall catalytic activity are their structure, Si/Al ratio, particle size, and nature of the exchanged cation.

It is well known that some of the inorganic constituents of biomass including alkali metals and alkaline earth metals act as a catalyst during the thermal degradation process that can determine the rate of degradation and yield of char in pyrolysis. To study the effect of the acidity of Y zeolites, sodium, calcium and magnesium cation forms were investigated as these alkaline earth metals are indigenous to a variety of biomass. Broido et al. proposed that the mechanism of thermal decomposition of the biomass during pyrolysis is affected by the alkali metal cations present and make the natural polymer chains by fragmentation of the monomers. Raveendran et al. [15] claimed that it's the cations rather than anions of alkali metals that are mainly affecting the catalytic pyrolysis of biomass. In the present work, Y zeolite was prepared with different acidities by exchanging cations and used for in-situ biomass catalytic pyrolysis to investigate the effect of acidity and cation forms of Y zeolite on biomass pyrolysis and properties of bio-oil. H-ZSM5 is a well-known catalyst used for cracking, deoxygenation and synthesis of aromatic hydrocarbons, and it is investigated in current work to study the effect of different zeolite structure on biomass pyrolysis and bio-oil properties.

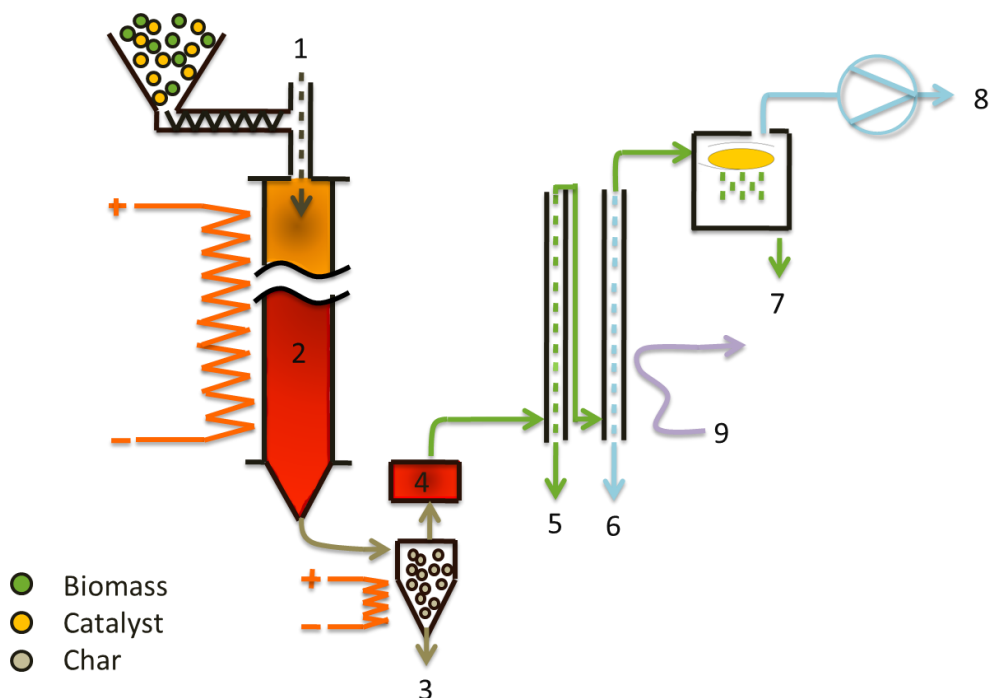
Fractionation of the bio-oil vapors by staged condensation at the downstream of the pyrolysis process is an option to tailor the bio-oil composition. Fractionation of the bio-oil can also be achieved for example by distillation, but re-heating of the bio-oil results in the formation of cross-linked solid carbonaceous residues because of the high reactivity of some fractions present in the bio-oil. There is very limited research available on fractionation during condensation of biomass pyrolysis vapors, Westerhof et al. [16] studied the effect of the condenser conditions on the water and organics content in the liquid obtained in the first condenser. Effendi et al. [17] studied the fractional condensation to concentrate phenolic compounds in a targeted fraction of the bio-oil. Oasmaa et al. [18] studied the fractional condensation to remove the light fractions from the bio-oil and found an increase the stability the bio-oil when the light fraction was replaced by an alcohol. In presented work, the online fractionation of catalytic pyrolysis vapors was used to improve overall quality of bio-oil, including its water content, elemental composition and calorific value. Online fractionation was employed using two condensers operated at different temperatures to produce two different liquids, organic rich and aqueous rich.

A bench scale unit consisting of an entrained flow downer reactor system is designed for in-situ catalytic flash pyrolysis of biomass. The entrained flow downer reactor type is selected because it characterizes easy operation handling, and demonstrates high heating rates of the biomass while maintaining good control of the reaction conditions for instance the residence time of reactants and products [19, 20]. Experiments were conducted for in-situ upgrading of pyrolysis vapor with premixed feedstock of catalyst and biomass,

using different cation forms of Faujasite zeolites, different zeolite structures (MFI zeolites), different reaction temperatures and different catalyst to biomass ratios. Furthermore, results of fractional condensation are presented where flash pyrolysis, catalytic upgrading and fractional condensation are integrated in a single pyrolysis system.

### 3.2 Materials and Methods

A continuous bench scale unit of 1 kg/h feedstock (biomass or/and catalyst) capacity has been used catalytic flash pyrolysis of woody biomass. The experimental set-up used was described in detail in an earlier publication [21], the schematic of the unit is presented in **Figure 7**. An entrained flow reactor of cylindrical quartz tube of 4.2 m length with an internal diameter of 50 mm is used for in-situ catalytic flash pyrolysis to produce bio-oil. The catalyst and biomass are mixed before feeding to pyrolysis unit. The residence time of biomass and pyrolysis products in the reactor is controlled with nitrogen carrier gas. The vapors, gases and solids leaving the reactor enter tangentially into a cyclone that allows removal of solids particles up to 20  $\mu\text{m}$ . The solids consist of char (ash and unconverted biomass) for non-catalytic experiments, and char plus spent catalyst for in-situ catalytic experiments. Due to a wide particle size distribution of the biomass and the catalyst, fine particles are separated in a hot filter element at the downstream of the cyclone. Solids recovery system allows complete removal of char and catalyst. Knowing the concentration of catalyst in biomass and the amount of feedstock consumed for each experiment, the amount of catalyst in the solids can be determined.



**Figure 7:** Schematic presentation of the experimental setup; 1. Carrier Gas (N<sub>2</sub>). 2. Pyrolysis Reactor 3. Solids recovery. 4. Hot particle filter element. 5-6-7. Liquid collection 8. Gas to analysis unit. 9. Coolant.

The condensation unit consists of two double tube heat exchangers that are operated with a coolant mixture of glycol and water at  $-5\text{ }^{\circ}\text{C}$ , the bio-oil fractions are collected together from both condensers except for online fractionation experiments. When fractionation of pyrolysis vapors is required, tap water is used in first condenser instead of glycol/water mixture and water flow rate is controlled to set desired temperature of the outlet gas/vapor stream, the second condenser is operated with coolant at  $-5\text{ }^{\circ}\text{C}$  to for maximum recovery of liquid. The light and heavy fractions of bio-oil are recovered in first and second condenser respectively, and collected separately from both condensers. Separation of light fraction from bio oil can improve its quality because the light fraction carries mainly the water and oxygenate components. In this two-step condensation scheme, major portion of the condensable is recovered. Other operating conditions and parameters are listed in **Table 8**.

**Table 8:** Operating conditions

Reactor temperature	400-550 $^{\circ}\text{C}$
Reactor pressure	1 atm
Feed hopper capacity	4 kg
Feedstock feed rate	1 kg/h
Biomass particle size range	150-1000 $\mu\text{m}$
Vapor residence time in reactor	2-4 sec

### 3.2.1 Product analysis

The non-condensable gases mainly composed of carbon dioxide, carbon monoxide and C1, C2, C3 hydrocarbons. The volumetric flow rate of these gases is measured with a gas flow meter and a sample of this stream is pumped to an on-line gas analysis unit. Infrared analyzers are used to measure CO, CO<sub>2</sub> and an FID analyzer is used to measure hydrocarbons. The elemental composition of the liquid is analyzed with a thermoscientific elemental analyzer. The water contents of the oil are quantified by Karl Fisher titration, and a bomb calorimeter is used to determine the heating value of the bio-oil. An Agilent GC-MS is used to analyze the bio-oil and the NIST8 library is used to detect the components.

### 3.2.2 Biomass

The biomass used for the experiments consisted of wood fibres commercially available with trade name LIGNOCEL by J. RETTENMAIER & SÖHNE GmbH. The biomass particle size varied from 0.1 to 1 mm. The ultimate and proximate analyses are presented in **Table 9**.

**Table 9:** Ultimate and proximate analysis; and bio-chemical composition of biomass

	C	H	N	O <sup>3</sup>	Moisture	Volatiles	Fixed C.	Ash	LHV
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[MJ/kg]
Lignocel	49.2	5.7	0.1	45.0	6.5	76.4	13.6	3.5	16.6

Bio-chemical composition of biomass [16]	(wt.%, dry)
Cellulose	35
Hemicellulose	29
Lignin	28

### 3.2.3 Catalysts:

Solid acids Faujasite (Y and MFI ZSM5) zeolites were used which catalyze de-oxygenation, basic properties of these catalysts are presented in **Table 10**. The Faujasite zeolites were used in different cation forms, H-Y and Na-Y were obtained from Zeolyst International, Ca-Y and Mg-Y were prepared by Petrobras, Brazil by ion exchange of Na-Y zeolite. H-ZSM5 was obtained from Albemarle B.V. All the catalysts were in powder form, with a particle size ranging between 5  $\mu\text{m}$  to 50  $\mu\text{m}$ .

## 3.3 Results and Discussion

Preliminary experiments were conducted to optimize the operating conditions e.g. the solids residence time and reaction temperature ( $T = 450 - 550$  °C, 2 secs < residence time < 4 sec) for a maximum solid conversion and liquid yield. In all these tests the stability of the unit was satisfactory and reproducible experiments could be performed for 1 to 2 hours. A reasonably good mass balance around 90% and liquid yields around 60% were achieved.

An optimum liquid yield was obtained at 500 °C reactor temperature and 4 seconds vapors residence time in the reactor. Maximum biomass conversion was achieved at 4 seconds vapor residence time, vapor residence times longer than 4 seconds did not improve the biomass conversion and had negative effect on pyrolysis products. Longer vapor residence time caused significant increase in production of gases and water contents of the liquid due to undesired secondary cracking of bio-oil vapors. For catalytic experiments, these operating conditions were fixed in order to compare the effect of catalyst yield and characteristics of biomass pyrolysis products. Catalytic experiments were performed with a premixed feedstock of biomass and catalyst. The two step condensation scheme was

<sup>3</sup> by difference

employed for fractional condensation of bio-oil to separate the organic and aqueous rich phases of bio-oil.

**Table 10:** Properties of zeolite catalysts

Catalyst	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	Nominal form	Na <sub>2</sub> O [Weight %]	Surface Area [m <sup>2</sup> /g]	Manufacturer
H-ZSM5	23	H <sup>+</sup>	0.05	425	Albemarle
H-Y	5.2	H <sup>+</sup>	0.2	660	Zeolyst International
Na-Y	5.1	Na <sup>+</sup>	13.0	900	Zeolyst International
Mg-Y	5.1	Mg <sup>2+</sup>	-	-	Petrobras
Ca-Y	5.1	Ca <sup>2+</sup>	-	-	Petrobras

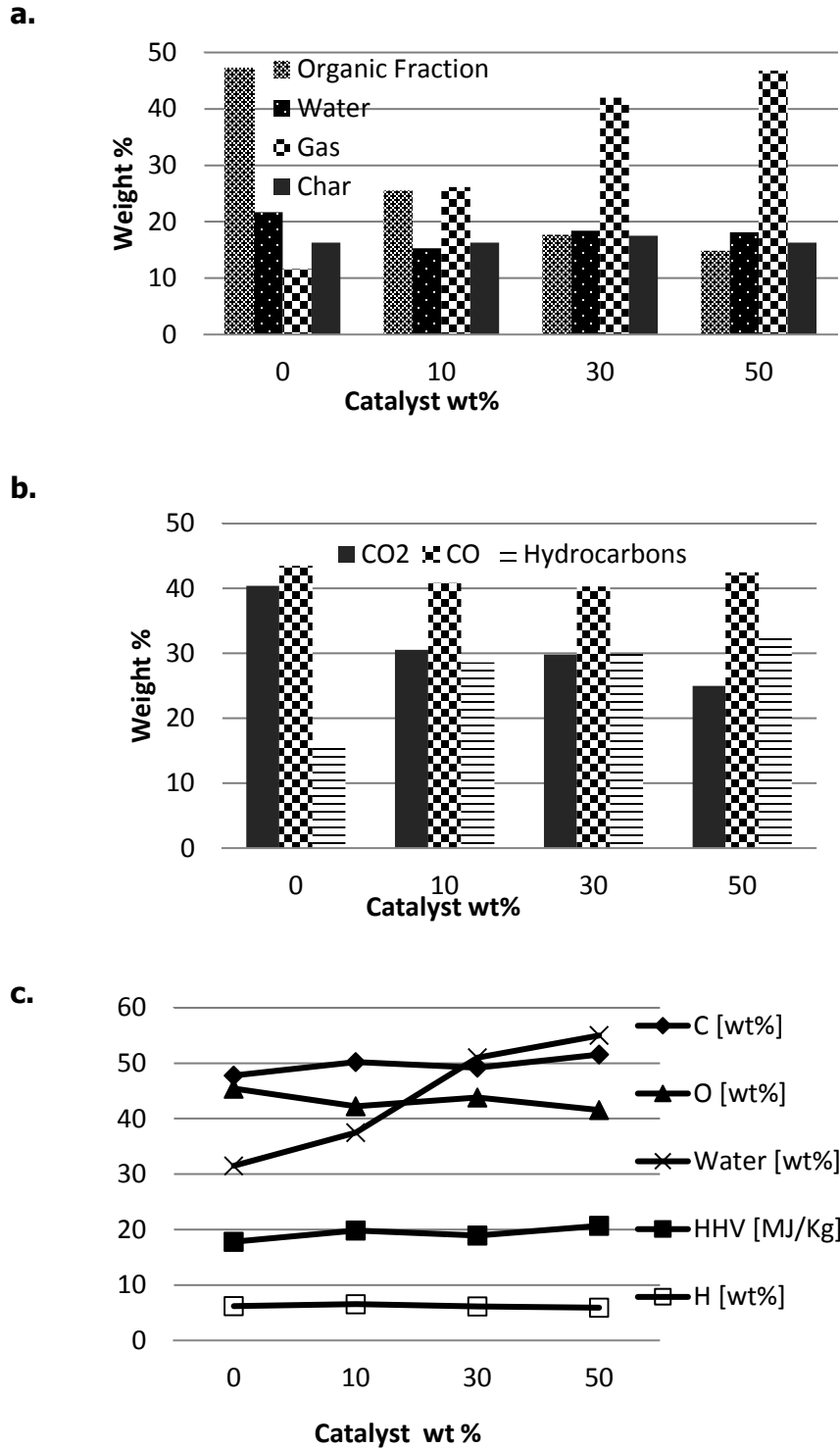
### 3.3.1 Effect of the catalyst to biomass ratio:

For heterogeneous catalytic systems, the contact between catalyst and biomass/vapor is an important issue and poses practical challenges. The contact can be improved by increasing the catalyst to biomass ratio. ZSM5 and Y zeolites were used to study the effect of the catalyst to biomass ratio on the yield and properties of the pyrolysis products. . The results are presented separately for both catalyst types in sub section 3.1.1 and 3.1.2., respectively.

#### 3.3.1.1 Effect of the H-ZSM5 to biomass ratio:

To study the effect of the H-ZSM5/biomass ratio on the yields and characteristics of the pyrolysis products, experiments were performed with mixture of 0, 10, 30, and 50 weight % of H-ZSM5, and 100, 90, 70 and 50 weight % of biomasses, respectively. H-ZSM5 and biomass were physically mixed and this premixed feedstock was used for in-situ catalytic pyrolysis. Bio-oil was collected in one condenser (no fractionation) and its water content was determined b by Karl Fisher titration, and the organic and water contents/fractions of the bio-oil are presented separately for a better comparison.

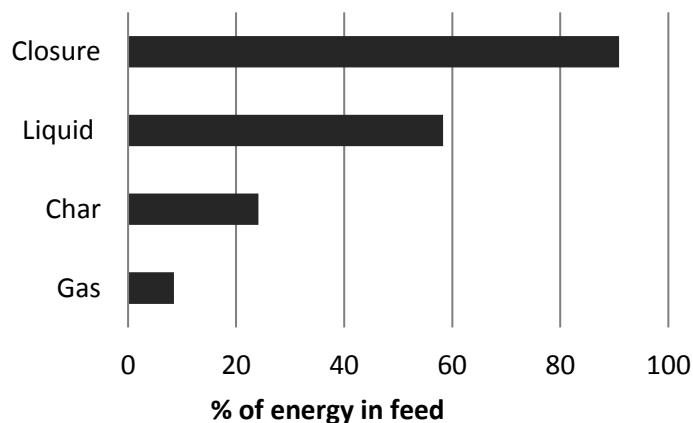
The catalyst/biomass ratio had a significant effect on the yields of the different pyrolysis products (see **Figure 8a**). A higher catalyst/biomass ratio led to an increase in the gas production while the organic liquid fraction significantly reduced. Using 50% H-ZSM5, the organic liquid fraction reduced from 47.2% to 14.9% and the gas fraction was increased from 11.6% to 46.8% compared to the non-catalytic experiment.



**Figure 8:** a. Effect of the H-ZSM5/biomass ratio on pyrolysis products yields. b. Effect of the H-ZSM5/biomass ratio on the gas composition. c. Effect of the H-ZSM5/biomass ratio on the characteristics of the bio-oil

The catalyst/biomass ratio had no significant effect on the char content. The gas composition is presented in **Figure 8b** as relative selectivity to CO, CO<sub>2</sub> and hydrocarbons. H-ZSM5 had a significant effect on the gas composition compared to the non-catalytic situation but changing the catalyst/biomass ratio did not alter the gas composition to a great extent. A biomass mixture with 50% H-ZSM5 produced a gas with 32.5 % hydrocarbons and a relative concentration of CO<sub>2</sub> and CO of 25% and 42.5%. A high catalyst/biomass ratio enhanced the secondary cracking of the oil vapors and caused formation of hydrocarbon gases. Increasing the H-ZSM5 concentration did not result in de-oxygenation of the bio-oil vapor via the preferred route of de-carboxylation, but a significant amount of oxygen is released via de-carbonization as CO gas. During catalytic de-oxygenation of bio-oil vapors, the oxygen may be given off by de-hydration, de-carbonization and de-carboxylation leading to the formation of water, CO and CO<sub>2</sub>, respectively.

A detailed analysis of bio-oil is presented in **Figure 8c**. The elemental composition and higher heating value of bio-oil is given on dry basis. H-ZSM5 caused an increase in the carbon and a decrease in the oxygen content, while the hydrogen content remained the same. At 50% H-ZSM5 concentration, the oxygen content of bio-oil is reduced from 45.4% to 41.6% and the higher heating value increased from 17.8 to 20.7 MJ/kg. Although this is a minor difference, a considerable difference in physical appearance of the bio-oil could be noted. The thermal pyrolysis oil was highly viscous and heavy tar was observed in the condenser, while the bio-oil obtained via catalytic pyrolysis was less viscous and no heavy fraction was observed in condensers. Obviously, the heavy fraction of the bio-oil was cracked to lighter fractions and gaseous components for high catalyst concentrations.



**Figure 9:** Energy balances as % of energy in feed for non-catalytic pyrolysis of biomass

Energy balance for non-catalytic pyrolysis of biomass is presented in **Figure 9**. Energy yields for each product were calculated from the mass yields (see **Figure 8**, non-catalytic pyrolysis experiment) and the gross energy contents, or higher heating values (HHV) of the corresponding products. HHV for liquid and char was measured and calculated for the gas stream. A good closure of energy balance was achieved. The optimum type of catalytic

pyrolysis reactor should have an integrated heat recovery system from combustible gases, and char and can increase the overall process efficiency and economics.

### **3.3.1.2 Effect of Na-Y to biomass ratio:**

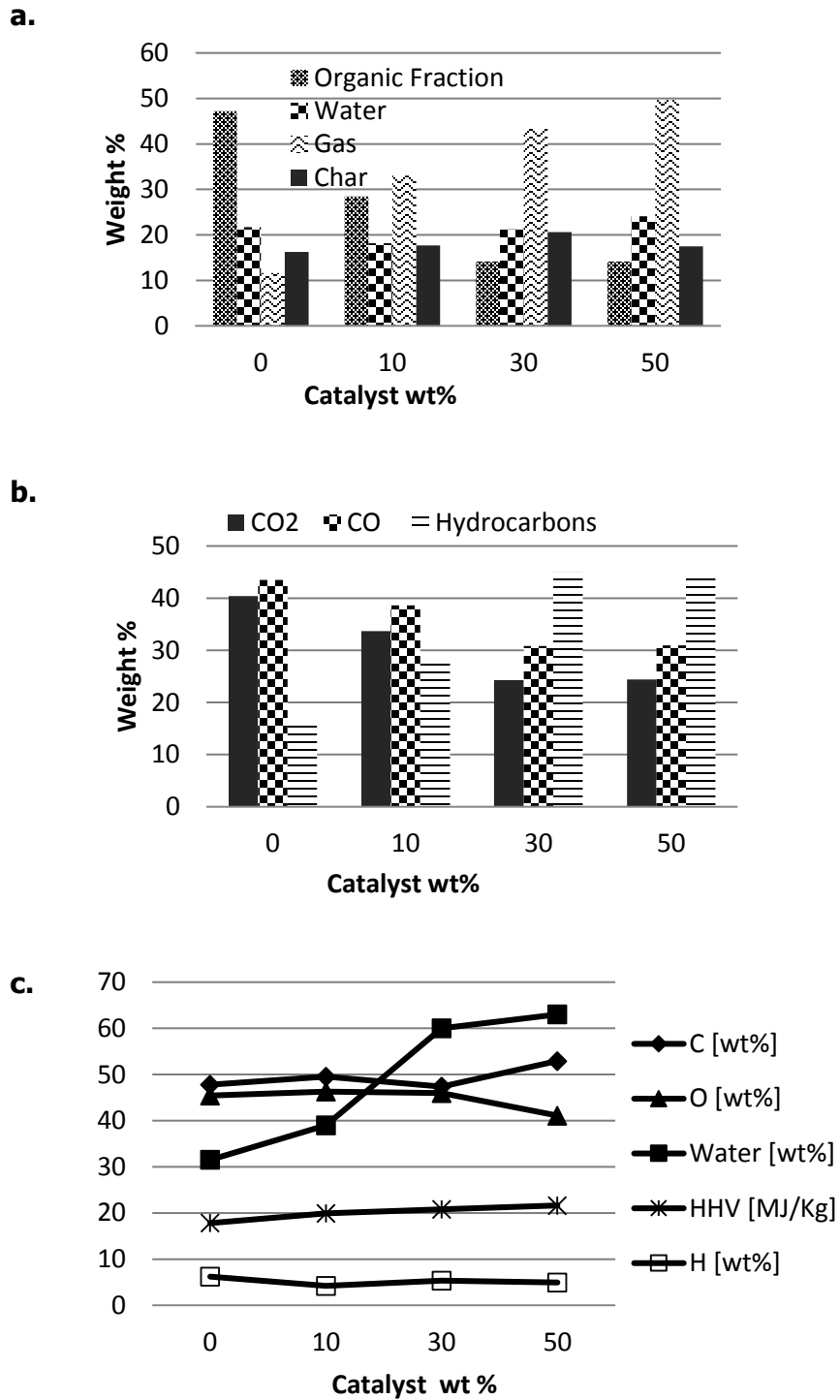
To study the effect of the Faujasite zeolite/biomass ratio on product yields (liquid, gas and char) and on the liquid product characteristics, experiments were performed using 0, 10, 30, and 50 weight % of Na-Y zeolite. The product yields are presented in **Figure 10a** and the results show that an increasing Na-Y/biomass ratio had a significant effect on the product yields. The trends are like those of H-ZSM5. A higher Na-Y/biomass ratio resulted in more formation of gas and a lower organic fraction yield. For 50% Na-Y, the organic liquid fraction reduced from 47.2% to 14.1% and the gas yield increased from 11.6% to 49.7% and there was no considerable change in the char yield compared to non-catalytic pyrolysis. The gas composition is presented in **Figure 10b**. For 50% Na-Y, the hydrocarbons concentration in the gas increased from 16.1 % to 44.7% while the CO<sub>2</sub> and CO concentration decreased from 40.4% and 43.5% to 24.4% and 31% respectively compared to the non-catalytic experiment. A higher Na-Y/biomass ratio favored the secondary cracking of vapors and the effect is larger than it was in case of H-ZSM5. The bio-oil analysis is presented in **Figure 10c**. For 50% Na-Y in the biomass mixture, the oxygen content of the bio-oil is reduced from 45.4% to 41.1% and the higher heating value of the bio-oil increased from 17.8 to 21.6 MJ/kg compared to the non-catalytic situation.

The experimental results show that an increasing catalyst/biomass ratio enhanced the formation of gas and lowered the organic fraction yield. The higher gas yields in presence of the H-ZSM5 and Na-Y catalysts are due to the secondary cracking and de-oxygenation reactions of the product vapors. Oxygen is removed as CO and CO<sub>2</sub> and hydrocarbon gases are produced as a result of the cracking reactions. The lower organic liquid yield due to gas formation is compensated by the better quality. The thus produced could be used for e.g. local electricity production in a gas engine.

### **3.3.2 Effect of the catalytic pyrolysis reaction temperature:**

To investigate the effect of the reaction temperature on the catalytic flash pyrolysis process, experiments were conducted with 50% H-ZSM5 at 550 °C and 500 °C. The product yields and composition of the gaseous products are compared in **Table 11** while the characteristics of the bio-oil are presented in **Table 12**, respectively. Increasing the reaction temperature caused a decrease in the organic liquid yield and an increase in the gas yield. It is evident from the gas composition that a higher reaction temperature enhanced the secondary cracking of the bio-oil vapors resulting in a lower yield of organic liquid. A lower char yield at a higher temperature is expected because elevated reaction temperatures are favorable for a better conversion of lignin components in the biomass. A higher reaction temperature resulted in a significant increase in the higher heating value of the bio-oil (22.6 MJ/kg) because of a higher deoxygenation achieved, but this improvement is at the costs of a lower yield of organic liquid.





**Figure 10:** a. Effect of the Na-Y/biomass ratio on pyrolysis products yields. b. Effect of the Na-Y/biomass ratio on the gas composition. c. Effect of the Na-Y/biomass ratio on the characteristics of the bio-oil

**Table 11:** Effect of the pyrolysis reaction temperature on different pyrolysis products yields and gas composition

50% H-ZSM5	Organic Fraction	Water	Gases	Char	C <sub>x</sub> H <sub>y</sub>	CO <sub>2</sub>	CO
500 °C	14.9	18.2	46.7	16.3	32.5	25	42.5
550 °C	9.9	18.0	62.7	12.0	45.2	17.3	37.5

**Table 12:** Effect of the pyrolysis reaction temperature on the characteristics of the liquid the liquid<sup>4</sup>

	C	H	O	Water	HHV
	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
500 °C- 50% H-ZSM5	47.2	4.9	46.8	55.0	20.7
550 °C - 50% H-ZSM5	50.7	4.9	42.5	64.5	22.6

### 3.3.3 Effect of zeolite structures:

To investigate the effect of different zeolite structures such as Faujasite (H-Y) and MFI (Pentasil/H-ZSM5), experiments were performed with H-Y zeolite and the results were compared with those with H-ZSM5. For comparison 50 weight % of catalyst was used for this series of experiments to observe the clear effect of the zeolite structure. The product yields (dry basis), gas composition and liquid characteristics for 50% H-Y are compared with the results obtained for H-ZSM5 in **Figure 11a**, **Figure 11b**, and **Figure 11c**.

It can be seen that H-Y produced much less gas resulting in a higher yield of organic liquid. H-Y produced less hydrocarbon gas and more CO and CO<sub>2</sub> gas; this is the preferred route for de-oxygenation of the bio-oil vapors to keep maximum hydrogen and carbon in the bio-oil. It is evident that H-Y is less prone to secondary cracking of the oil vapors.

A major difference between both catalysts structures becomes clear from the liquid characteristics. H-Y was more effective for the de-oxygenation of the bio-oil vapors and lowered the oxygen content of the bio-oil to 41.7, and increased the carbon and hydrogen content of the bio-oil to 56.2 and 5.2 wt.%, respectively. For 50% H-Y the heating value increased from 17.8 to 22.9 MJ/kg compared to non-catalytic experiment. This higher heating value can be attributed to the changed elemental composition of the bio-oil. H-Y has a superior performance compared to H-ZSM5 with respect to the energy recovery in the bio-oil. H-Y produced an organic liquid with a higher yield and higher calorific value, and with lower water content. A detailed comparison of the two zeolite structures is carried out in paragraph 3.5 based on the chemical composition of the produced bio-oils.

### 3.3.4 Effect of varying acidities of Faujasite zeolite:

<sup>4</sup> The elemental composition and higher heating value of the bio-oil are presented on dry basis

The nature of the (exchanged) cation is a key property of Faujasite zeolite catalysts and it influences the acidity of zeolite and its catalytic activity. To investigate the effect of varying acidities of Faujasite zeolite on catalytic biomass pyrolysis, experiments were performed with Mg-Y and Ca-Y, and a comparison was made with H-Y, Na-Y and non-catalytic experiments. For all these experiments 50 wt.% of catalyst was used in the biomass mixture. The acidity of Y zeolite is changed in the order of H-Y > Na-Y > Mg-Y > Ca-Y. The product yields (dry basis), gas composition and liquid characteristics are presented in **Figure 11a**, **Figure 11b**, and **Figure 11c**.

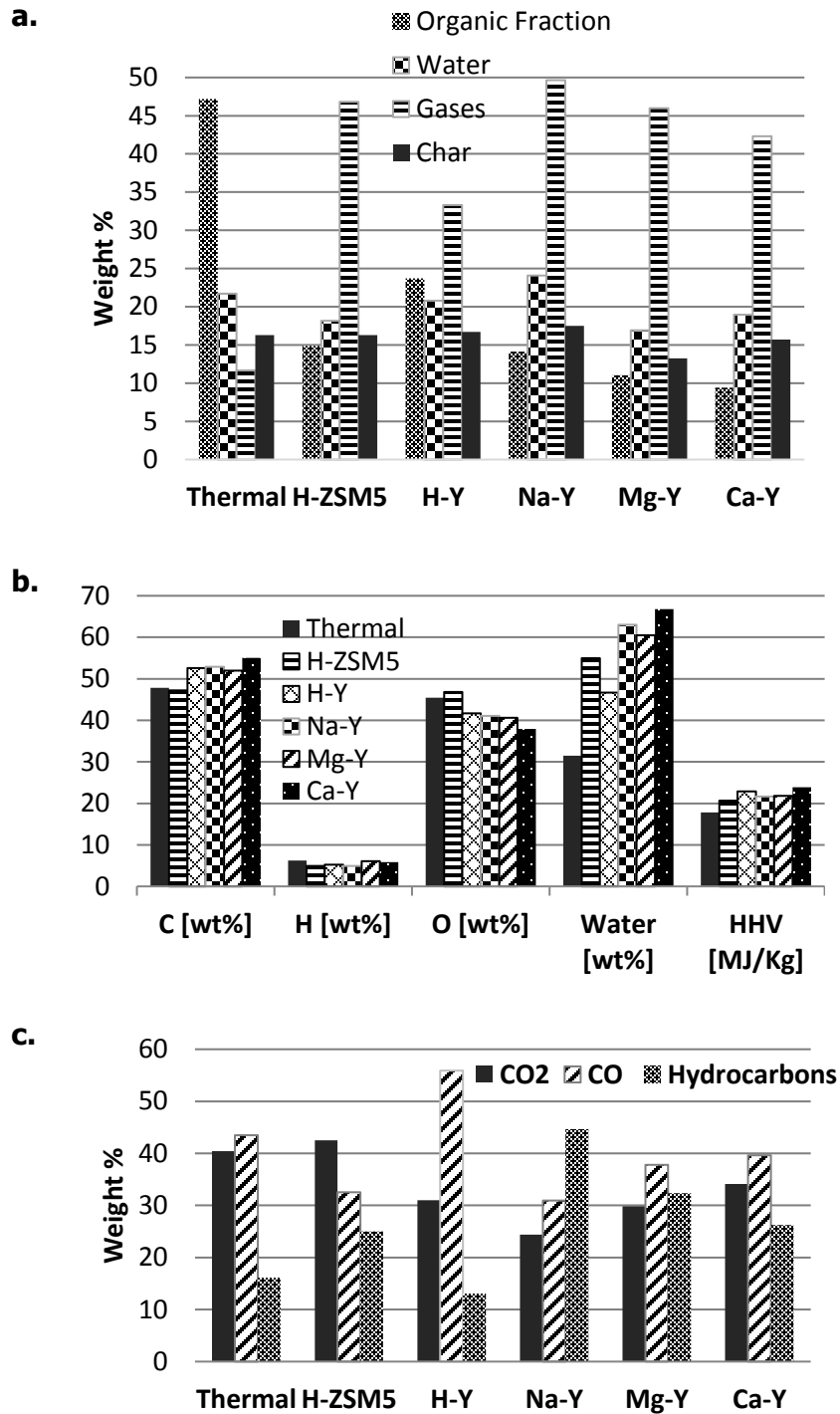
Compared to the non-catalytic experiment, all cation forms of Faujasite zeolites produced less organic liquid and more gas. Among the all Faujasite zeolites, H-Y produced the lowest amount of gas and highest amount of organic liquid. Reducing the acidity of Y zeolite resulted in more CO and CO<sub>2</sub> formation and fewer hydrocarbons in the gas, except for H-Y. H-Y produced the highest amount of CO and lowest amount of hydrocarbon gas while the production of CO<sub>2</sub> was quite like other zeolites.

The liquid product is not very different in terms of elemental composition. The oxygen content slightly decreased with a reducing acidity of Y zeolite while the carbon content increased in all cases. Acidic zeolite, H-Y, showed a superior performance compared to the other zeolites in terms of keeping the energy in the liquid product. It produced the highest amount of organic liquid with almost similar elemental composition, slightly lower calorific value and lower water formation compared to the other zeolites.

### 3.3.5 Chemical Characterization of liquid

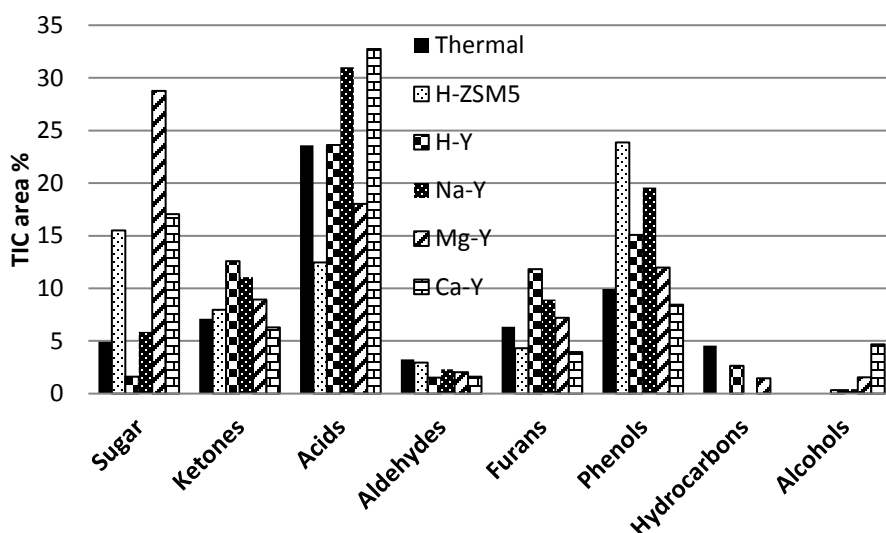
The bio-oil obtained from the catalytic and non-catalytic pyrolysis experiments was diluted in acetone and analyzed in a GC-MS. A wide range of organic compounds are found in the bio-oil. In **Figure 12**, the chemical composition of the bio-oil has been described and the compounds have been classified according to their chemical nature as hydrocarbons, phenols, furans, acids, alcohols, aldehydes, ketones, sugars and aromatics.

Hydrocarbons are assumed to be the desirable fractions since they are chemicals with a high commercial value. In addition to the hydrocarbons, compounds like phenol and its alkylated derivatives also have a high value, especially for the resin or adhesive industry and they could make the pyrolysis process economically more feasible. Furans are stable compounds with a high energy value and fuel compatible. While the oxygen-containing compounds, such as acids and carbonyls, are considered as undesirable fractions. The reduction of the acids is important factor to improve the corrosive nature of the bio-oil and the reduction of carbonyls is important for its stability. These two factors are critical with respect to handling, storage and fuel applications of the bio-oil. A catalyst is expected to produce more desirable and less undesirable compounds in the bio-oil.



**Figure 11:** a. Effect of zeolite structure and varying acidities of Y zeolite on pyrolysis products yields. b. Effect of zeolite structure and varying acidities of Y zeolite on the characteristics of the bio-oil. c. Effect of zeolite structure and varying acidities

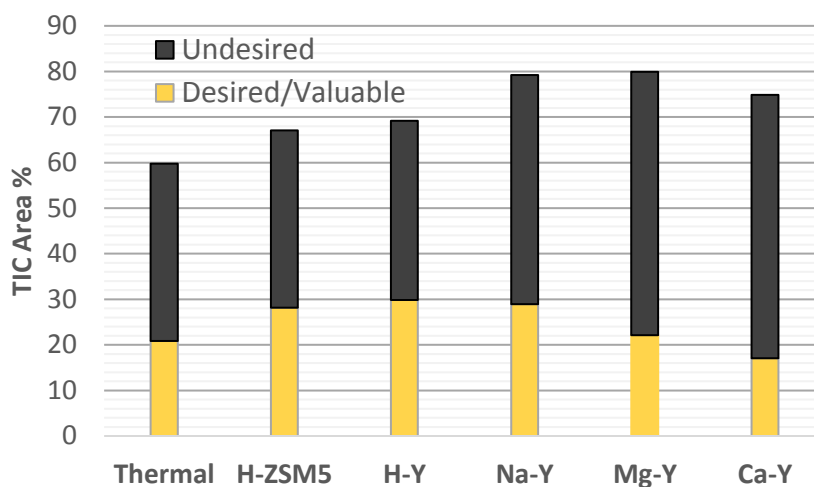
Acids, phenols, ketones and furans were the dominating groups of bio-oil and acetic acid was the single most dominant and undesired compound in the bio-oil. In general it can be said that increasing the acidity of the zeolite catalyst lowered the acid yields except for Mg-Y. H-ZSM5 has the highest acidity among the investigated zeolites and produced the lowest amount of acids. The acid yield was reduced to half of what was obtained during non-catalytic pyrolysis. Increasing the acidity of zeolites enhanced the formation of ketones except for H-ZSM5. H-Y produced the highest amount of ketones and Ca-Y formed the lowest amount of ketones. All zeolites reduced the amount of aldehydes in the bio-oil, and the effect was more pronounced for lower acidities of the zeolites, except for H-Y that produced the least amount of aldehydes. Increasing the acidity of the zeolites favored the production of furans except for H-ZSM5. Both H-ZSM5 and Ca-Y produced the lowest amount of furans. Reducing the acidity of zeolites favored the formation of valuable alcohols, and Ca-Y produced the highest amount of alcohols. Compared to the non-catalytic runs, the application of zeolite catalysts increased the production of phenols, a valuable commodity for resins and adhesive industry. In general, increasing the acidity of zeolites favored the phenols production except for H-Y. Zeolites did not favor the production of hydrocarbons i.e. the important compound for fuel application. Only H-Y zeolite was able to almost completely convert the sugar components.



**Figure 12:** Chemical composition of the bio-oil obtained by non-catalytic and catalytic pyrolysis of biomass

To evaluate the overall performance of the zeolite catalysts and the effect of their acid nature on the chemical composition of the bio-oil, the chemical compounds are grouped in so called undesired and desired/valuable compounds (see **Figure 13**). Acids, ketones, aldehydes and sugars are grouped as undesired compounds, while hydrocarbons, phenols, furans and alcohols are grouped as desired and valuable compounds. Compared to the non-catalytic (thermal) experiments, both H-ZSM5 and H-Y were successful in enhancing the yields of the desired components and reducing the undesired components in the bio-oil. Na-Y also produced a high amount of desired compound but also enhanced the formation of undesired compounds. Reducing the acidity of Y-zeolite had a negative effect

on the bio-oil composition and produced less desired compounds and more undesired compounds. Summarizing it can be stated that H-Y produced a bio-oil with both a high chemical and calorific value in combination with a high organic liquid yield. H-Y has a high potential for the production of a high quality fuel via catalytic flash pyrolysis of lignocellulosic biomass. H-ZSM5 is a very close competitor of H-Y but it results in a lower yield of organic liquid.



**Figure 13:** Effect of catalyst on the desired and undesired compounds of the bio-oil

The result obtained in this study with zeolite catalysts in an entrained flow reactor are comparable to other studies conducted at bench scale units. Aho et al. [22] performed catalytic pyrolysis of pine wood in a fluidized bed reactor to investigate the effect of different structures of acidic zeolite catalysts. H-Y and H-ZSM5 were tested as catalysts and the chemical composition of the bio-oil was found to be dependent on the structure of acidic zeolite catalysts. H-Y zeolite and H-ZSM5 catalyst significantly reduced the organic liquid yield. The formation of acids and alcohols over H-ZSM5 was lower while the formation of ketones was higher than over the H-Y zeolite. Lappas et al. [23] used FCC and H-ZSM5 for catalytic flash pyrolysis of biomass in a circulating fluid bed reactor with continuous solids regeneration. The effect of specific operating variables including the type of catalyst and the catalyst/biomass ratio on the final liquid product quality and yield was studied. FCC and H-ZSM5 catalysts produce high gas yields, with dominating oxygenated gaseous compounds as CO<sub>2</sub> and CO. A high catalyst to biomass ratio enhanced the production of additional water and resulted in a lower yield of organic liquid obtained with less oxygenated compounds but no improvement in the calorific value. H-ZSM5 produced more carbonyls while the production of acids, HCs, phenols and heavy oxygenates was not significantly changed. Atutxa et al. [24] also reported that bio-oil from catalytic pyrolysis with H-ZSM5 was less oxygenated than oil from thermal pyrolysis. Atutxa et al. used a conical spouted bed reactor to investigate catalytic pyrolysis of pine wood at 400 °C and found a substantial increase in gaseous products (mainly CO<sub>2</sub> and CO) and water, and a corresponding decrease in the organic liquid and char yield compared to thermal pyrolysis. The obtained liquid product was less corrosive and more stable than thermal bio-oil.

It can be concluded that in general zeolites reduce oxygenates compounds in the bio-oil via various routes of de-oxygenation e.g. de-hydration, de-carbonylation and de-carboxylation. However, main drawback of the zeolites for catalytic pyrolysis is a significant decrease in bio-oil organics yield due to the increase in the production of gases, water and coke. Organics yield in the bio-oil can be increased if deep cracking and formation of hydrocarbon gas can be avoided, it may be controlled by manipulating the strength and concentration of acid sites in zeolites.

### 3.3.6 Online fractionation via staged condensation of pyrolysis vapors:

Online fractionation via two staged condensation of pyrolysis vapors was employed to investigate the possibilities to improve the composition and thus the quality of the bio-oil. The pyrolysis vapors leaving the pyrolysis reactor were condensed via two condensers at different temperatures. The first condenser was used to condense the heavy and middle fractions of the bio-oil and it was operated at an outlet temperature of 55 °C. The second condenser was used to condense the water and light oxygenate fractions of the bio-oil and operated with a coolant (glycol/water) temperature of -5 °C resulting in an outlet gas temperature of 6-8 °C. The fractionation experiments were performed with 50% Na-Y and 50% H-ZSM5 and the liquid characteristics from the first condenser are compared with the results of the experiments without fractionation in **Table 13**.

**Table 13:** Liquid Characteristics for experiments with and without fractionation<sup>5</sup>

Exp. #	Description	C	H	O	Water	HHV
		[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
1	Na-Y (no Fractionation)	52.9	4.9	41.1	63.0	21.6
2	Na-Y-1st Condenser	53.6	6.5	39.9	31.0	23.1
3	H-ZSM5(no Fractionation)	51.6	5.9	41.6	55.0	20.7
4	H-ZSM5-1st Condenser	55.4	6.2	37.9	11.0	23.0

Experiment 1 and 3 were performed with both condensers at the same low temperature and the liquid was collected together (no fractionation), while experiment 2 and 4 were performed two staged condensation. For the fractionation experiments, the liquid obtained in the second condenser was mainly water: more than 90 wt.% water content and it was not possible to perform a reliable and accurate elemental analysis of the liquid because of the high water content. The liquid obtained from the first condenser was rich in organic compounds and its characteristics are presented here in table 13 being the fraction of interest. A significant difference in the composition of the bio-oil is seen in case of

<sup>5</sup> The elemental composition and higher heating value of the liquid are presented on dry basis

fractionation. In case of Na-Y and fractionation, the water content goes down to 31 wt.%, the hydrogen content increased, and the higher heating value of the bio-oil increased to 23.1 MJ/kg.

In case of H-ZSM5, fractionation experiment was more effective and resulted in a bio-oil with a water content of 11 wt.%. The oxygen content of the bio-oil decreased to 37.9 wt % while both the hydrogen and carbon content increased. The higher heating value of the bio-oil increased to 23 MJ/kg, this effect can be attributed to the concentration of lignin derivatives in the bio-oil that are mainly condensed in the second condenser, the lignin derivatives contains a relative low oxygen compared to the light organic compounds. The GC/MS analysis of the water-rich liquid collected from the second condenser (see **Table 14**) revealed that acetic acid and furfural were the most dominating components in the liquid, and they contributed up to 60% of the organic fraction of the liquid collected in second condenser. The remaining 40% of the liquid mainly consisted of ketone and phenol groups. In general, online fractionation was effective to concentrate the high calorific value compounds of the bio-oil in the first condenser and the water and oxygenated compounds in the second condenser. The online fractionation could be cheap downstream approach to improve the quality of the bio-oil. Operating the first condenser at higher temperatures generates a bio-oil with upto 90 wt.% organics, which could be promising fraction for gasoline production via e.g. FCC, hy-drotreatment. The decrease in the oxygen content and the increase in the carbon and hydrogen content of the bio-oil could help to reduce the amount of hydrogen needed in case of e.g. hy-drotreatment of this bio-oil. The aqueous rich fraction of the pyrolysis liquid, obtained in the second condenser, contains upto 10 wt % light organics and could be an interesting raw stock for further extraction applications or for supercritical water gasification to produce hydrogen for hydro-treatment of the bio-oil [22, 23]

### 3.4 Conclusions

The bench scale unit can be operated successfully for in situ catalytic flash pyrolysis of biomass. The unit demonstrated a good operating stability and flexibility for varying operating conditions. The bio-oil recovery system provides the possibility for fractionation of different bio-oil fractions and adds-up to the degree of freedoms available for tailoring bio-oil properties.

Zeolites based acidic catalysts can perform de-oxygenation, at the cost of reduced organic liquid yield because of secondary cracking reaction of vapors leading to formation of gases. Nevertheless, the gas or char generated during the catalytic pyrolysis can supply a part of heat required for the pyrolysis step in an integrated process or it can be used for biomass drying. In general, increasing the acidity of zeolites favored the formation of desired compounds such as phenols and furans and reduced the most deleterious components in the bio-oil such as acids. However some of the undesired components in the bio-oil such as ketones, aldehydes increased with increasing acidity of zeolites.

Online fractionation via staged condensation was a successful technique to produce high calorific value bio-oil with very low water content of 10 wt.%. It can be concluded that fractionation is a promising cheap downstream approach to control the bio-oil properties.



The integrated process of catalytic pyrolysis and in-situ fractionation can be used for the production of tailor made biofuels and/or biochemical. The good quality bio-oil produced by integrated catalytic pyrolysis of biomass may be used as a co-feedstock for conventional refineries and existing infrastructure can be used for the production of sustainable transportation fuels.

**Table 14:** Component concentration of the aqueous fraction from the second condenser

Chemical Compound	TIC area %	
	H-ZSM-5	Na-Y
2-Butenal	3.6	2.8
<b>Acetic acid</b>	<b>28.1</b>	<b>37.1</b>
2-Isopropoxyethylamine	1.7	1.3
Butanedial	-	4.9
2-Cyclopenten-1-one	3.5	2.7
<b>Furfural</b>	<b>25.5</b>	<b>19.3</b>
2-Propanone, 1-(acetyloxy)-	-	1.8
2-Cyclopenten-1-one, 2-methyl-	2.5	-
5,9-Dodecadien-2-one, 6,10-dimethyl-, (E,E)-		2.0
4(3H)-Pyrimidinone	-	1.6
2-Furancarboxaldehyde, 5-methyl-	1.9	1.5
2-Cyclopenten-1-one, 3-methyl-	2.3	1.8
Butyrolactone	4.1	3.1
2(3H)-Furanone	3.7	2.8
2H-Pyran-2-one	1.6	1.2
1,2-Cyclopentanedione, 3-methyl-	3.0	2.2
Phenol	3.2	2.4
Phenol, 2-methoxy-	4.1	3.1
Phenol, 2-methyl-	2.1	1.6
Phenol, 4-methyl-	1.6	1.2
2-Methoxy-5-methylphenol	1.8	2.3
Phenol, 2,4-dimethyl-	1.6	-
Phenol, 2,6-dimethoxy-	4.0	3.0

### 3.5 References

1. Nokkosmäki, M.I., et al., *Catalytic conversion of biomass pyrolysis vapours with zinc oxide*. Journal of Analytical and Applied Pyrolysis, 2000. **55**(1): p. 119-131.
2. Mohebbali, G. and A.S. Ball, *Biocatalytic desulfurization (BDS) of petrodiesel fuels*. Microbiology, 2008. **154**(8): p. 2169-2183.
3. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.
4. Scholze, B. and D. Meier, *Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FTIR, and functional groups*. Journal of Analytical and Applied Pyrolysis, 2001. **60**(1): p. 41-54.
5. Sharma, R.K. and N.N. Bakhshi, *Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals*. The Canadian Journal of Chemical Engineering, 1991. **69**(5): p. 1071-1081.
6. Bridgwater, A.V., *Catalysis in thermal biomass conversion*. Applied Catalysis A: General, 1994. **116**(1-2): p. 5-47.
7. Maggi, R. and B. Delmon, *Characterization and upgrading of bio-oils produced by rapid thermal processing*. Biomass and Bioenergy, 1994. **7**(1-6): p. 245-249.
8. Maggi, R. and B. Delmon, *A review of catalytic hydrotreating processes for the upgrading of liquids produced by flash pyrolysis*, in *Studies in Surface Science and Catalysis*, B.D. G.F. Froment and P. Grange, Editors. 1997, Elsevier. p. 99-113.
9. Piskorz, J., et al., *Conversion of lignins to hydrocarbon fuels*. Energy & Fuels, 1989. **3**(6): p. 723-726.
10. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. Biomass and Bioenergy, 2012. **38**(0): p. 68-94.
11. Bridgwater, A.V. and M.L. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading*. Energy & Fuels, 1992. **6**(2): p. 113-120.
12. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts*. Journal of Analytical and Applied Pyrolysis, 2008. **81**(1): p. 72-79.
13. Lappas, A.A., et al., *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
14. Sadeghbeigi, R., *Chapter 1 - Process Description*, in *Fluid Catalytic Cracking Handbook (Second edition)*, R. Sadeghbeigi, Editor. 2000, Gulf Professional Publishing: Houston. p. 1-39.
15. Raveendran, K., A. Ganesh, and K.C. Khilar, *Influence of mineral matter on biomass pyrolysis characteristics*. Fuel, 1995. **74**(12): p. 1812-1822.
16. Westerhof, R.J.M., et al., *Controlling the Water Content of Biomass Fast Pyrolysis Oil*. Industrial & Engineering Chemistry Research, 2007. **46**(26): p. 9238-9247.
17. Effendi, A., H. Gerhauser, and A.V. Bridgwater, *Production of renewable phenolic resins by thermochemical conversion of biomass: A review*. Renewable and Sustainable Energy Reviews, 2008. **12**(8): p. 2092-2116.
18. Oasmaa, A., et al., *Quality Improvement of Pyrolysis Liquid: Effect of Light Volatiles on the Stability of Pyrolysis Liquids*. Energy & Fuels, 2005. **19**(6): p. 2556-2561.

19. Biagini, E., M. Cioni, and L. Tognotti, *Development and characterization of a lab-scale entrained flow reactor for testing biomass fuels*. *Fuel*, 2005. **84**(12–13): p. 1524-1534.
20. Brown, A.L., et al., *Design and Characterization of an Entrained Flow Reactor for the Study of Biomass Pyrolysis Chemistry at High Heating Rates*. *Energy & Fuels*, 2001. **15**(5): p. 1276-1285.
21. Imran, A., et al., *High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate*. *Fuel Processing Technology*, 2014. **127**(0): p. 72-79.
22. Demirbas, A., *Hydrogen Production from Biomass via Supercritical Water Gasification*. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2010. **32**(14): p. 1342-1354.
23. Guo, Y., et al., *Review of catalytic supercritical water gasification for hydrogen production from biomass*. *Renewable and Sustainable Energy Reviews*, 2010. **14**(1): p. 334-343.



## CHAPTER 4:

# High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate<sup>6</sup>

**Abstract:** Performance of a novel alumina-supported sodium carbonate catalyst was studied to produce a valuable bio-oil from catalytic flash pyrolysis of lignocellulosic biomass. Post treatment of biomass pyrolysis vapor was investigated in a catalyst fixed bed reactor at the downstream of the pyrolysis reactor. In-situ catalytic upgrading of biomass pyrolysis vapor was conducted in an entrained flow pyrolysis reactor by feeding a premixed feedstock of the catalyst and biomass.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  was very effective for de-oxygenation of the pyrolysis liquid and oxygen content of the bio-oil was decreased from 47.5 wt.% to 16.4 wt.%. An organic rich bio-oil was obtained with 5.8 wt.% water content and a higher heating value of 36.1 MJ/Kg. Carboxylic acids were completely removed and the bio-oil had almost a neutral pH. This bio-oil of high calorific low, low water and oxygen content may be an attractive fuel precursor. In-situ catalytic upgrading of biomass pyrolysis vapor produced a very similar quality bio-oil compared to post treatment of pyrolysis vapors, and shows the possible application of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  in a commercial type reactor system such as a fluidized bed reactor.

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## 4.1 Introduction

Pyrolysis-oil (hereinafter "bio-oil") produced with current flash pyrolysis technologies is not suitable for direct use as a transportation fuel or as a fuel additive. The presence of oxygenated compounds in the bio-oil mainly contributes to its deleterious properties, high viscosity, non-volatility, high acidity and resulting corrosiveness and extreme instability upon storage, lower energy density than the conventional fuel by 50%, incompatibility and immiscibility with fossil fuels, thermal instability and tendency to polymerize under exposure to air [1-5]. Catalytic de-oxygenation is considered as a first line option to overcome the problem characteristics of the bio-oil beside catalytic reformation of the large lignin derived molecules into useful products.

The challenge in de-oxygenation catalyst development is to design a catalyst that selectively removes the problematic oxygenates in the bio-oil. The oxygen may be given off by de-hydration, de-carbonylation and de-carboxylation leading to the formation of water, CO and CO<sub>2</sub>, respectively. The de-carboxylation is the preferred route for de-oxygenation in comparison to de-hydration as de-carboxylation allows retention of hydrogen in bio-oil, maximizes oxygen removal with minimal carbon loss and thereby increases heating value, decreases the aromatic compounds, minimizes the water content of the bio-oil, and decreases its hydrophilicity. Hence, in order to retain maximum energy content in the bio-oil, selective scission of bonds should follow the order of C-C > C-O > C-H.

So far, catalyst studies for biomass pyrolysis have been mainly focused on zeolites (Y, ZSM-5, Mordenite and Beta), and mesoporous aluminosilicates, However, zeolites and aluminosilicates have not shown any promising results. Major drawbacks to use relatively small pore zeolites are; a significant decrease in organics yield due to the increase of the production of water and gases, and a rapid catalyst deactivation by coke deposition [6]. Alkali metals are found to be effective catalysts for H<sub>2</sub>O and CO<sub>2</sub> gasification of carbon [7]. Lee et al. used Na<sub>2</sub>CO<sub>3</sub> for the catalytic gasification of rice straw over nickel catalyst and formation of gas was significantly enhanced [8]. The effect of alkali compounds on the properties of bio-oil has not been studied systematically and there is very limited literature available on effect of alkali compounds on bio-oil. Several researchers [9-12] used alkali compounds as a catalyst for biomass pyrolysis and found that alkali compounds lowered the temperatures of biomass devolatilization and decreased biomass conversion time, these effects were enhanced by increasing the basicity of alkali compound and the use of the Na with respect to the K ion. Bradbury et al. found that the inorganic content in the biomass has significant effect on yield of gas and char, and concluded that the increasing the inorganic contents in the biomass promotes the secondary cracking reactions that leads to break down of higher molecular compounds to smaller ones [13]. It is well known that cations of alkali metal in biomass can effect thermal decomposition mechanism of fast pyrolysis and can form the natural polymer chains via primarily fragmentation of the monomers [14]. Raveendran et al. claimed that the alkaline cations have a significant effect on the catalytic pyrolysis of biomass compared to anion of alkali metals [15].

Alkali metals can be applied directly for catalytic biomass pyrolysis but direct addition of alkali metal catalysts has several disadvantages, e.g. difficult and expensive recovery of

the catalyst. To solve these problems, they can be supported on a catalyst carrier e.g. alumina and taking advantage of catalytic effects of both alumina and alkali metal. Very few studies could be found on active alumina which is a solid acid catalyst [16, 17]. Larger pore size alumina has potential for reducing the coke formation and enhancing the organic liquid yield due to their lower acidity. Larger molecules, particularly lignin-derived compounds, can enter, reformulate and exit the bigger pores of alumina with lesser chances of coke formation and resulting blockage of the pores. To take advantage of larger pore size alumina and alkali metal, a novel alumina-supported sodium carbonate ( $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ) catalyst is developed based on systematic studies at laboratory scale with batch experiments using a 2 gram biomass sample and a catalyst fixed bed reactor [18]. In current work,  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  has been implemented in a bench scale unit of 1 kg/h biomass capacity that consists of an entrained flow pyrolysis reactor. Post pyrolysis vapor treatment was carried out in a catalytic fixed bed reactor to study the effect of the catalyst temperature independent of the pyrolysis reaction and to isolate the catalyst/vapor contact problems may occur in case of in-situ application of the catalyst in entrained flow pyrolysis reactor. In-situ upgrading of pyrolysis vapor was carried out in the entrained flow pyrolysis reactor with premixed feedstock of catalyst and biomass to simulate the condition of a commercial system such as fluidized bed reactor. The entrained flow downer reactor configuration is selected because of easy operation handling and it demonstrated high heating rates of the biomass while maintaining good control of the reaction conditions for instance the residence time of reactants and products [19, 20].

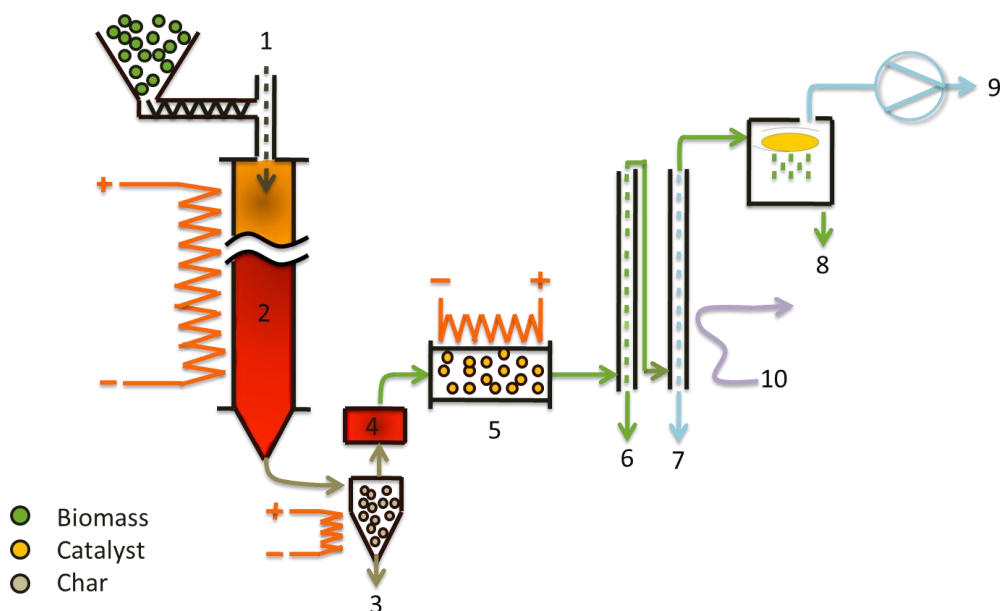
## 4.2 Materials and methods

To produce bio-oil via catalytic flash pyrolysis of woody biomass, a continuous bench scale unit of 1 kg/h feedstock (biomass/and catalyst) capacity has been designed. A schematic of the unit is presented in **Figure 14**. The feedstock (biomass or biomass/catalyst) is loaded into the feed hopper and fed to the entrained down flow reactor by screw feeder and inert carrier gas (Nitrogen). The pyrolysis reactor is consisted of a cylindrical quartz tube of 4.2 m length with an internal diameter of 5 cm. The reactor is heated electrically through heating coils around the wall and the reactor temperature is controlled by thermocouples installed at various heights of the reactor. Feedstock enters the reactor at its top, and in a few seconds the thermo-chemical conversion of biomass particles takes place under inert atmosphere yielding a gas composed of condensables (bio-oil), non-condensables, and char.

The catalyst fixed bed reactor was used only for the post treatment of pyrolysis vapor and it was bypassed for in-situ upgrading of pyrolysis vapor in entrained flow reactor. The fixed bed reactor is made of stainless steel, 300 cm length and 6 cm internal diameter. The reactor is heated electrically and the catalyst is loaded before the start of the experiment. The vapor residence time in the catalyst fixed bed reactor is less than half a second.

The vapors, gases and solids leaving the reactor enter tangentially into a cyclone that allows removal of solids particles up to 20  $\mu\text{m}$ . The solids consist of char (ash and unconverted biomass) for non-catalytic experiments and char plus spent catalyst for in-situ catalytic experiments. Due to a wide particle size distribution of the biomass and the

catalyst, it is difficult to design a very efficient cyclone, therefore fine particles are separated in a hot filter element at the downstream of the cyclone. A solid free gas is carried to two double tube heat exchangers (operated with a coolant mixture of glycol and water at  $-5\text{ }^{\circ}\text{C}$  circulating through outer tubes). In this section the condensable fraction of the gases is recovered as a liquid. Heavy and middle fractions of the condensable vapors are recovered in first condenser and lighter fraction of the bio-oil is recovered in second condenser. The gases leaving the condensers still carry a mist or fumes of product vapors that are recovered in a rotating particle separator (RPS) where they are impinged onto the surface of filter and can flow downwards out of the filter by gravity as a liquid. The oil separated by the filter element is collected at the bottom of the RPS and taken off at the end of the test run. The RPS is very efficient to capture the mist of oil vapors and nearly vapor free gas leaves the RPS and is taken off for gas analysis. Other operating conditions and parameters are listed in **Table 8**.



**Figure 14:** Schematic presentation of the experimental setup; 1. Carrier Gas (N<sub>2</sub>). 2. Pyrolysis Reactor 3. Solids recovery. 4. Hot particle filter element. 5. Catalyst fixed bed reactor. 6-7-8. Liquid collection 9. Gas to analysis unit. 10. Coolant.

#### 4.2.1 Biomass

The biomass used for the experiments consisted of wood fibres commercially available with trade name LIGNOCEL by J. RETTENMAIER & SÖHNE GmbH. The biomass particle size varied from 0.1 to 1 mm. Ultimate and proximate analysis and bio-chemical composition of biomass are presented in **Table 9**.

#### 4.2.2 Catalyst

Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was prepared by wet impregnation method. A Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> ratio of 1:2 by weight was used. Na<sub>2</sub>CO<sub>3</sub> (ACS reagent grade >99.5%) and γ-Al<sub>2</sub>O<sub>3</sub> was obtained from Sigma Aldrich and Albemarle respectively. A saturated solution of sodium carbonate was



prepared at room temperature (21 g Na<sub>2</sub>CO<sub>3</sub> per liter of water) and heated to 60 °C. Alumina carrier ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was added to the Na<sub>2</sub>CO<sub>3</sub> solution and stirred for 2 hours keeping at 60 °C. After two hours, the catalyst was dried in an oven at 105 °C to evaporate the water. Finally, the catalyst was calcined in an oven at 600 °C for 12 hours and stored in a desiccator. Catalyst characterization has been described in detail by Nguyen et al. [18].

### 4.2.3 Product analysis

The non-condensable gases leaving the RPS primarily composed of carbon dioxide, carbon monoxide and C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> hydrocarbons. The volumetric flow rate of these gases is measured with a gas flow meter and a sample of this stream is pumped to an on-line gas analysis unit. Infrared analyzers are used to measure CO, CO<sub>2</sub> and a FID analyzer is used to measure hydrocarbons. The liquid is analysed with an elemental analyser to find out elemental composition. Water contents of the oil are quantified by Karl Fisher titration. A bomb calorimeter is used to determine the heating value of the bio-oil. An Agilent GC-MS is used to analyse the bio-oil and the NIST8 library is used to detect the components.

## 4.3 Results and discussion

For thermal (non-catalytic) pyrolysis experiments, the targeted maximum liquid yield was obtained at 500 °C reactor temperature and 4 seconds residence time of biomass/vapors in the reactor. Therefore, same operating conditions were used for the catalytic experiments in order to compare the effect of catalyst on nature and yield of different products of biomass pyrolysis. Catalytic experiments were conducted both for post treatment of biomass pyrolysis vapor in a catalyst fixed bed and for in-situ upgrading of pyrolysis vapor in an entrained flow reactor.

### 4.3.1 Post treatment of biomass pyrolysis vapors in a catalytic fixed bed reactor

A series of preliminary experiments was conducted to optimize the pyrolysis reaction conditions in the entrained flow reactor and the targeted maximum liquid yield was obtained at 500 °C reactor temperature and 4 seconds residence time of biomass/vapors. The produced vapor/gas stream was passed over a fixed bed of 200 gram of Na<sub>2</sub>CO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. A catalyst/biomass ratio of 1:1 was used for present experiments. To achieve desired catalyst/biomass ratio, an experimental run was set to feed 200 gm of biomass to achieve 1:1 ratio of catalyst and biomass. Furthermore, a slight reduction in catalyst activity was observed due to coke formation at the catalyst when more than 200 gm of biomass was fed in a single batch of experiment. The catalyst requires a continuous combustion of coke to maintain its activity that was not possible in current experimental scheme.

To study the effect of catalyst on biomass pyrolysis, several experiments were conducted with the fixed bed catalyst at 500 °C. The product yields on basis of dry initial weight of biomass are presented in **Table 15**. In contrast to thermal pyrolysis, catalytic pyrolysis resulted the phase separation of the liquid product; the liquid was instantaneously separated in aqueous and organic fractions upon condensation in the condenser. This

phase separation made it possible to separate the organic fraction from the aqueous fraction. The whole liquid was transported to a conical separation flask, and the organic fraction was settled at the bottom of the flask and collected separately from the aqueous fraction. For thermal experiment, the water content of the liquid has been represented as the aqueous fraction but in practice there was no phase separation achieved in the absence of the catalyst.

**Table 15:** Product yields weight (%) for both thermal and catalytic pyrolysis

	O.F <sup>7</sup>	A.F <sup>8</sup>	Coke	Char	Gas	C <sub>x</sub> H <sub>y</sub>	CO <sub>2</sub>	CO
Thermal	47.2	21.7	0	16.2	11.6	1.9	4.7	5.1
Catalytic (500 °C)	9.4	23	7.1	18.4	30.2	4	14.4	11.8

The implementation of the catalyst significantly altered the pyrolysis products. Total liquid was decreased from 58% to 32.4% and three times higher amount of gas was formed in presence of the catalyst. The yield of organic liquid fraction was considerably reduced to 9.4% compared to that of 47.2% in non-catalytic experiment. The catalyst also led to the conversion of a part of pyrolysis vapors into the coke. Nguyen et al. has described that this coke has high oxygen content up to 41.5 wt.% and high amount of coke formed on catalyst contributes as a major de-oxygenation route [18]. The catalyst did not have any influence on the char yields, the char was recovered before the catalyst bed and the catalyst could not influence the primary conversion of the biomass. The effect of the catalyst on the gas composition is presented as the relative selectivity to CO, CO<sub>2</sub> and hydrocarbons. The type of the gaseous products formed (CO, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>) indicates the energy content of the bio-oil after de-oxygenation and cracking. The formation of CO and CO<sub>2</sub> will lower the oxygen content of bio-oil and the formation of C<sub>x</sub>H<sub>y</sub> will lower the energy content of the bio-oil due to the loss of hydrogen. The catalyst favored the formation of CO<sub>2</sub> and suppressed the CO formation although the formation of hydrocarbon was unavoidable because of the secondary cracking of the vapors. The gas and the coke formation are the two major routes for the de-oxygenation and the reduction in the liquid yield is obvious, however further development of the catalyst can increase the liquid yield by minimizing de-hydration and cracking reaction and by maximizing the de-carboxylation reaction.

**Table 16** shows the product energy distribution of post vapor treatment experiment based on the energy in the biomass fed. Overall 78% of the energy was recovered in the products and 22% of the energy was unrecovered either lost in aqueous liquid fraction,

<sup>7</sup> Organic fraction of liquid

<sup>8</sup> Aqueous fraction of liquid

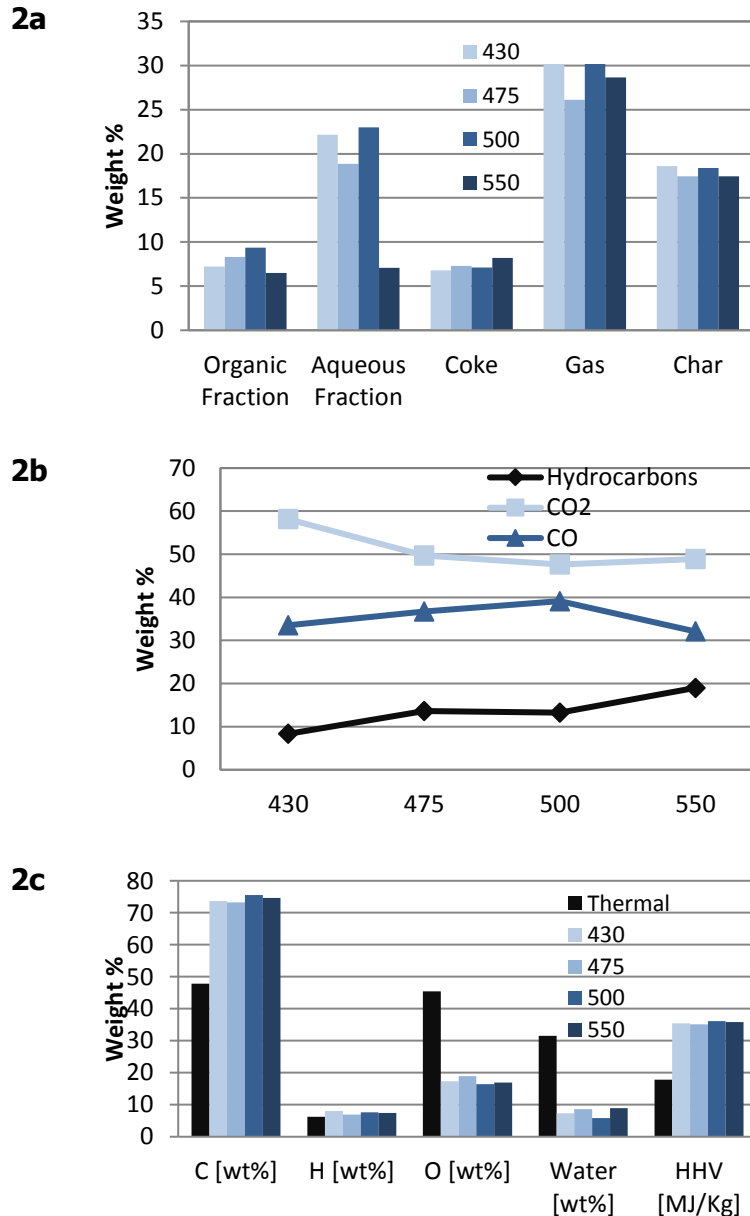
in conversion process or/and in missing mass. 20.9 % of the energy was recovered in the bio-oil. The energy recovery from the byproducts (char, coke and gas) can make the process economically attractive in an integrated pyrolysis system to provide the heat required for thermal conversion of biomass.

**Table 16:** % energy recovery of catalytic pyrolysis products

O.F	Coke	Char	Gas	Overall Energy Recovery
20.9	10.5	27.3	19.3	78

The catalyst bed temperature can be operated independent of the pyrolysis reactor temperature and experiments were performed at different catalyst bed temperatures to study the effect of the reaction temperature on the liquid product. The catalytic experiments were performed at a catalyst bed temperature of 430, 475, 500 and 550 °C and biomass pyrolysis products distribution and gas composition is presented in **Figure 15a** and **Figure 15b**. The catalyst bed temperature had a very little effect on the product distribution and the gas composition. The organic liquid yield slightly increased with increasing the catalyst bed temperature and highest organic yield achieved at 500 °C. Further increase in the catalyst bed temperature was not beneficial and had negative impact on the organic liquid yield. Optimum organic yield achieved at 500 °C catalyst bed temperature was 9.4% and corresponding aqueous fraction yielded 23%. With an increasing catalyst bed temperature, there was a slight increase in the coke yield and the highest coke yield obtained at 550 °C was 8.2 %. With increasing temperature from 430 °C to 500 °C, the hydrocarbons and CO concentration in the gas increased and decreased when the temperature was further increased to 550 °C. The effect of increasing catalyst bed temperature on CO<sub>2</sub> was vice versa, the CO<sub>2</sub> yield decreased by increasing catalyst bed temperature from 430 °C to 500 °C and then slightly increased when catalyst bed temperature was further increased to 550 °C.

As the organic liquid fraction called bio-oil is of main interest, a detailed analysis of the bio-oil is presented in **Figure 15c**. The aqueous fraction will be discussed later. The elemental composition and higher heating value of bio-oil are on dry basis. The catalyst application had a significant effect on the bio-oil properties and noticeable improvements in the bio-oil quality were achieved. No clear trends can be seen in the bio-oil properties with increasing catalyst bed temperature. As the maximum bio-oil yield was achieved at 500 °C with minimum oxygen content, it will be used for the comparison between the thermal and the catalytic pyrolysis experiments. Carbon content of the bio-oil increased from 46% to 75.5%, the hydrogen content increased from 6% to 7.6%. The water content of bio-oil decreased from 31.5 to 5.8% and the higher heating value increased from 17.8 MJ/kg to 36.1 MJ/kg. The most significant improvement was the high level of de-oxygenation achieved; 65% de-oxygenation was obtained as the oxygen content of the bio-oil decreased from 47.5% to 16.4%.



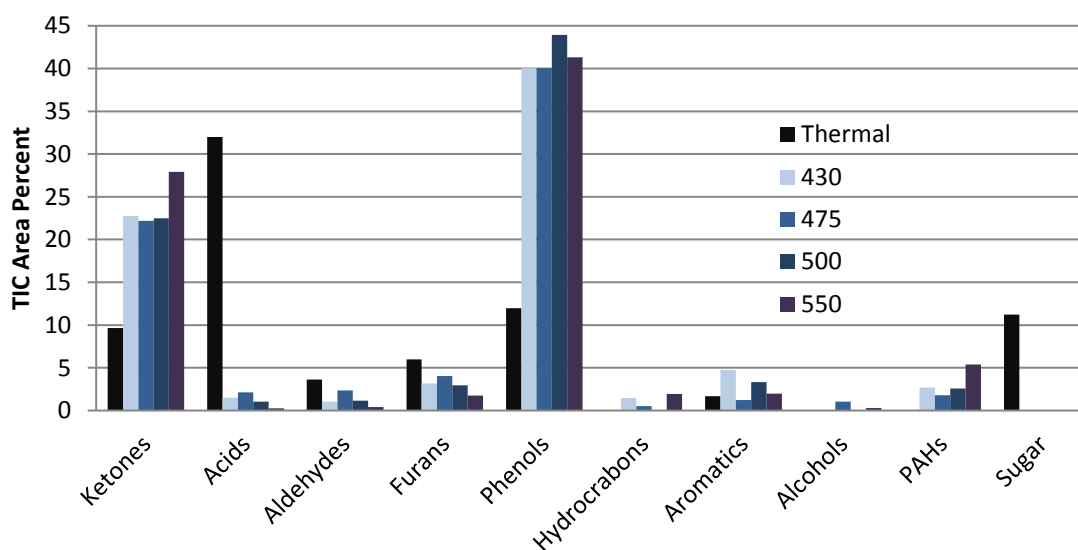
**Figure 15:** a. Effect of the catalyst bed temperature (°C) on the products yields b. Effect of the catalyst bed temperature (°C) on the gas composition c. Effect of catalyst bed temperature (°C) on the characteristics of organic fraction of the liquid

The experimental results show that  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  had desired effect on the properties of bio-oil and a high-quality bio-oil was achieved that can be further improved for fuel application.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  resulted in a very high de-oxygenation via gas and coke formation, although the bio-oil yield was lowered because of higher gas and coke formation but this lower bio-oil yield can be compensated by its superior quality, low oxygen contents and high energy density very close to that of fossil fuel.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  is an effective catalyst for de-oxygenation, it follows the ideal order of priority  $\text{CO}_2 > \text{CO} > \text{C}_x\text{H}_y$  aimed at removing maximum oxygen with single carbon atom and maximizing the

hydrogen content in the bio-oil. Higher gas yield in presence of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  are due to de-oxygenation and secondary cracking reactions of product vapors. Very low organic liquid yields obtained in the presence of the catalyst cannot be avoided if high de-oxygenation of the bio-oil is required because of the loss of carbon and hydrogen associated with various routes of catalytic de-oxygenation. The catalyst properties and process parameters may be further optimized to increase the bio-oil yield. An integrated heat recovery from combustible gases, char and coke can increase the overall process efficiency and economics.

### 4.3.2. Bio-oil characterization

The bio-oil obtained from the catalytic and non-catalytic pyrolysis of biomass was analyzed by GC–MS. As explained earlier whole liquid fraction was used for non-catalytic experiment and organic fraction (bio-oil) was used for catalytic experiment. A wide range of organic compounds are found in the bio-oil. The identified compounds of the organic phase are typically grouped as hydrocarbons, phenols, furans, carboxylic acids, alcohols, aldehydes, ketones, aromatics and PAHs (polycyclic aromatic hydrocarbons). In **Figure 16**, the chemical composition of bio-oil has been described as total ion chromatogram area percentages of all the compounds and the compounds have been classified according to their chemical nature.



**Figure 16:** GCMS analysis of the organic liquid fraction of thermal and catalytic pyrolysis (for catalytic post treatment of pyrolysis vapors)

There is no clear trend found in chemical composition of bio-oil with varying catalyst bed temperature but there was clear difference in catalytic and non-catalytic bio-oil. Carboxylic acids were most dominating compounds in non-catalytic bio-oil and acetic acid was the single most dominant compound found among all the acids.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  completely removed the acids from the bio-oil. This is the most significant improvement in quality of bio-oil as acids are the main contributor for acidity of the bio-oil [21] and removal of acids will lower the corrosivity and pH, and will improve the calorific value and handling properties of the bio-oil. Sugars being another contributor to the acidity of the bio-oil are

completely removed in the catalytic bio-oil. Removal of these two major contributors (acids and sugars) to the acidity of bio-oil is clearly reflected in acid measurements of the bio-oil presented in **Table 17**, and catalytic bio-oil is almost neutral in pH.

**Table 17:** Acidity of bio-oil

	Thermal	Catalytic at 500 °C
TAN <sup>9</sup>	159	3.45
pH	2.2-2.4	6.3

Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> caused a significant reduction in the aldehydes. Reduction in the aldehydes is very good for the stability and shelf life of the bio-oil. Complete removal of the acids and reduction in the aldehydes can be attributed to the intermediate acidity of the alumina, which seems to be optimum to inhibit some of undesirable reactions that lead to formation of acids and aldehydes.

Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> yielded high amounts of the phenols, a high value compound especially for resin and adhesive industry making the process economically attractive. Phenols are lignin derived product made by the cracking of the phenyl-propane units of the macromolecule lattice [21]. Huber et al. suggested that the aromatics, phenols and their alkyl substituted fractions are formed by recombination and cyclization reactions, via condensation from C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> fragments which are the initial degradation product [22]. Apparently, Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> favored the formation of substituted phenols, such as alkylated and alkoxyphenols.

PAHs and aromatic compounds in the bio-oil are considered lignin derived products mainly by the decomposition of polysaccharides. No PAHs are found in non-catalytic bio-oil. Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> formed PAHs, mainly naphthalenes and substituted naphthalenes while all fractions of aromatic compounds increased in the presence of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. It seems that Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> stimulated the catalytic reactions that favor the formation of PAHs such as cyclization, aromatization, condensation. Furthermore, alumina pores are large enough so that naphthalene and substituted naphthalenes can leave the pores after their formation before the polymerization of these products happened and caused coke formation. The large regular pores of alumina allow the diffusion of reactants in the catalyst and diffusion of the products out of catalyst, minimizing consecutive decomposition reactions [23]. The large pores of γ-Al<sub>2</sub>O<sub>3</sub> allow more molecules to enter the catalyst and experience the cracking and reforming reactions and their subsequent aromatization. It seems that the Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is able to catalyze reactions that can

<sup>9</sup> Total acid number of bio-oil based on standard ASTM 664

convert oxygenated compounds into aromatic hydrocarbons such as de-carboxylation, de-carbonylation, de-hydration and aromatization.

A noticeable effect was the increased formation of ketones in presence of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ . Ketones undergo condensation reactions and cause the formation of higher molecular weight components by polymerization reactions and increase viscosity [24]. Formation of ketones in presence of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  poses a challenge for the stability of the bio-oil. Ketones can be upgraded via post hydrogenation step to obtain liquid alkanes as described by Huber et al., this process involves aldol condensation and hydrogenation of ketones [22]. Nevertheless, increased ketones yield can be tolerated comparing the other benefits obtained in presence of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  for e.g. complete removal of acids, high heating value and high level of de-oxygenation.

The catalytic bio-oil obtained has a low water and oxygen content and is rich in organics which are attractive fractions for gasoline production via fluidized catalytic cracking (FCC)/hydrotreatment. The decrease in the content of oxygen, increase in hydrogen content and the concentration of molecules with more than six carbon atoms in the bio-oil could help to reduce the amount of hydrogen needed for the hydrotreatment of this bio-oil and make it an attractive precursor for fuel application.

#### 4.3.3. Characterization of the aqueous fraction

The aqueous fraction of the liquid obtained in the catalytic pyrolysis of biomass was analyzed for its water content and the chemical composition. The aqueous fraction consisted of 90-94% water (see **Table 18**) and the rest were organics. Due to the high water content of the aqueous fraction, the elemental composition cannot be obtained accurately. The organics present in the aqueous fraction are analyzed by GC-MS and compared with that of the bio-oil (organic fraction of the liquid) in

**Table 19.** For this comparison, experiment conducted at a catalyst bed temperature of 500 °C was selected. Compounds in the aqueous fraction are the same as the organic components in the bio-oil except for the ketones and phenols. The ketones yield is much higher in the aqueous fraction and lower in the organic fraction while the phenols are significantly lower in the aqueous fraction and higher in the organic fraction. Highly polarity ketones are originated from the cellulose and hemicellulose components of biomass [25] and phenolic compounds originates from lignin. Yields of other chemical compounds are altered only slightly. It is interesting to note that the catalyst has completely converted the acids as there is almost no acid found in both fraction of catalytically produced bio-oil. This complete removal of the acids can significantly improve the handling properties of bio-oil. The aqueous fraction could be interesting for extraction and supercritical water gasification to produce hydrogen for hydrotreatment of the bio-oil [26, 27].

#### 4.3.4 Catalyst regeneration characteristics

After each experiment, the catalyst was regenerated by combustion of the coke deposited on the catalyst. After the first regeneration, the catalyst showed an activity similar to the fresh catalyst. After the second regeneration, the catalyst showed some loss of activity

and partly irreversible deactivation of the catalyst happened. To study the deactivation behavior of the catalyst, experiments were performed with second time regenerated catalyst and results were compared with that of the fresh catalyst. Two experiments were performed at 475 °C and 500 °C catalyst bed temperature to study the catalyst deactivation behavior. Comparison of product distribution on dry basis is presented in **Figure 17a**. Second time regenerated catalyst shows similar trends at both reaction temperatures of 475 °C and 500 °C. A deactivated catalyst produced less coke and less gas and resulting in slightly higher liquid yields of both organic and aqueous fractions of the liquid. There was no noticeable difference obtained in gas composition using both fresh and deactivated catalyst at reaction temperatures of 475 °C and 500 °C.

**Table 18:** Water content of aqueous fraction of liquid obtained at different catalyst bed temperatures.

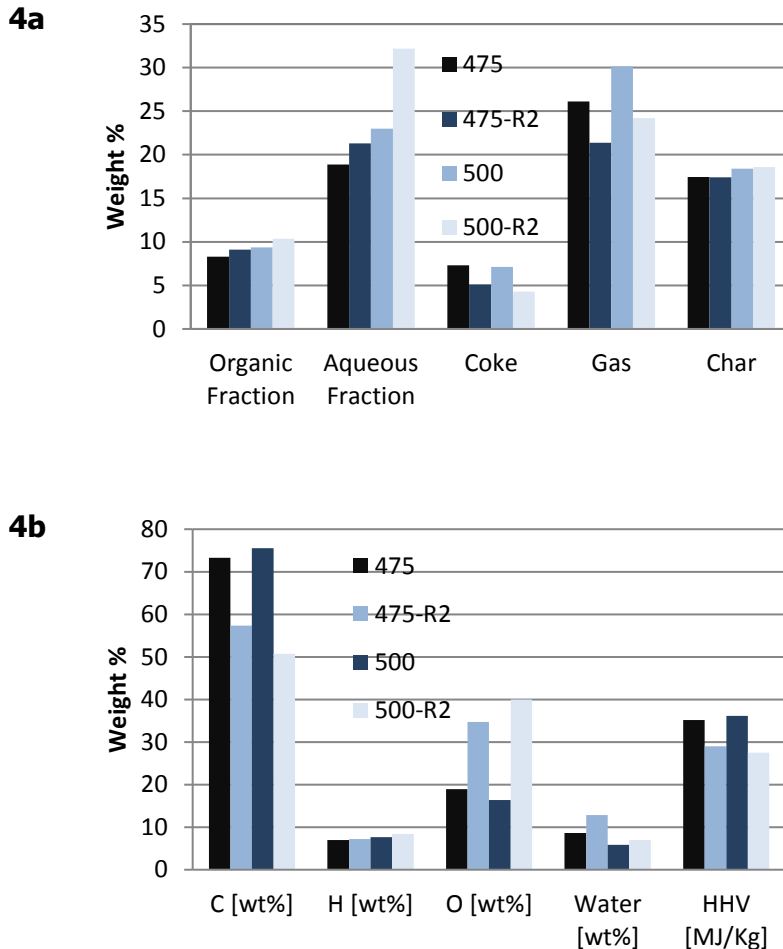
Catalyst temperature [°C]	Water content [wt.%]
550	90.7
500	93.7
475	91.4
430	92.9

**Table 19:** Comparison of organic compounds in the pyrolysis liquid.

	Ketones	Acids	Aldehydes	Furans	Phenols	Hydrocarbons	Aromatics	Alcohols	PAHs
Organic fraction	22.5	1.0	1.2	3.0	43.9	0.0	3.3	0.0	2.6
Aqueous fraction	55.8	1.7	0.5	3.3	11.3	1.2	0.0	2.0	0.0

A very significant difference was noticed in properties of the organic fraction of liquid (**Figure 17b**). Deactivated catalyst shows a relatively poor de-oxygenation of bio-oil. The catalyst used at higher reaction temperature showed a higher loss in its activity after regeneration. This loss in activity or deactivation of catalyst can be attributed to batch mode of catalyst application. As catalyst is employed for treatment of bio-oil vapors without continuous regeneration, the catalyst pores are completely blocked and shows irreversible deactivation. In a commercial application, catalyst will be employed with efficient and continuous regeneration system and irreversible deactivation of catalyst is not likely to happen but needs to be checked. If we take example of an FCC process, the small pores zeolites are successfully regenerated without loss of their catalytic activity. Alumina having even large pore size is likely to show even better performance in a FCC kind of process for treatment for of bio-oil vapors.





**Figure 17:** a. Effect of catalyst deactivation on yields of different products<sup>10</sup> b. Effect of catalyst deactivation on the characteristics of organic fraction of the liquid<sup>11</sup>

### 4.3.5 In-situ catalytic upgrading of biomass pyrolysis vapors in an entrained flow reactor system

In the previous section, results are presented for application of catalysts in a fixed bed reactor at the downstream of the pyrolysis reactor. The fixed bed catalyst system was used to isolate the catalyst/vapor contact problems may occur in case of in-situ application of the catalyst in an entrained down flow reactor, and to study the effect of the catalyst temperature independent of the pyrolysis reaction temperature. A fixed bed reactor system is not a viable option for commercial applications and also will result in problem with respect to continuous regeneration of the catalyst compared to more common

<sup>10</sup> Experiments 475 and 500 are conducted with fresh catalyst and 475-R2 and 500-R2 are conducted with second time regenerated catalyst.

<sup>11</sup> Experiments 475 and 500 are conducted with fresh catalyst and 475-R2 and 500-R2 are conducted with second time regenerated catalyst.

systems e.g. a fluid catalytic cracker (FCC) or a fluidized bed reactor system. Fluidized bed type systems are a common approach for catalytic pyrolysis of biomass at commercial scale, where the catalyst can partly or fully replace the heating media generally sand. To study in-situ catalytic flash pyrolysis of biomass,  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  was employed in an entrained down flow pyrolysis reactor. A good contact between the catalyst and the biomass is required for in-situ application. The catalyst was grounded and physically mixed with biomass in 1:1 ratio to have the same catalyst/biomass ratio that was used in the fixed bed catalysis. This premixed feedstock of biomass and the catalyst was fed to the pyrolysis reactor. As the temperature had not a significant effect on activity and function of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ , the in-situ catalytic pyrolysis experiments were conducted at 500 °C to optimize the biomass conversion and secondary cracking.

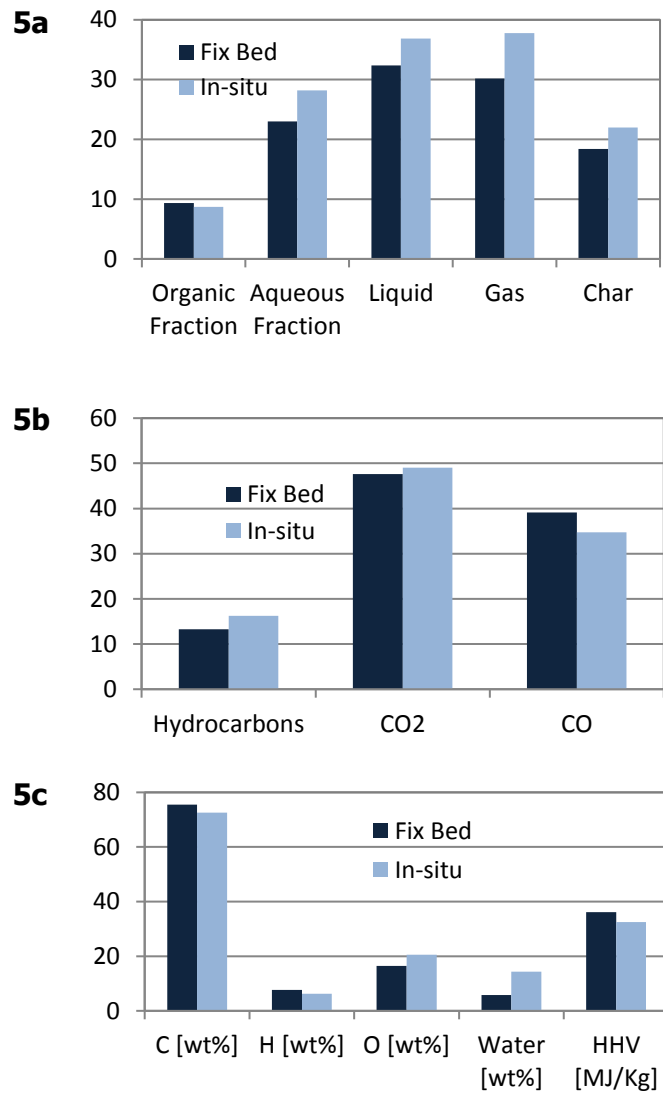
For comparison of fixed bed (post treatment) and in-situ application of catalyst, product distribution, gas composition and liquid characterization are presented in **Figure 18a**, **Figure 18b**, and **Figure 18c** respectively. In-situ experiments led to higher gas and char yields, higher liquid yields with higher aqueous fraction and slight lower organic fraction yields. A higher char yield for the in-situ experiments is attributed to the coke formation on the catalyst. A higher gas yield for the in-situ experiments can be attributed to a higher secondary cracking due to a longer contact of the catalyst and the vapors for in-situ mode where the vapor/solid residence time is 4 seconds being much longer than 0.5 second in the catalyst fixed bed in the post treatment mode. The lower organic liquid yields for in-situ experiments can also be attributed to this higher secondary cracking of the vapors. The bio-oil (organic liquid) characteristics show slightly less de-oxygenation for in-situ experiment, this can be attributed to the relative poor catalyst/vapor contact in the in-situ mode. A decrease in the carbon and hydrogen contents of the bio-oil can be noticed with resulting higher oxygen and lower energy contents of bio-oil. This loss in hydrogen and carbon in bio-oil is attributed to the higher yields of hydrocarbon gas.

A comparison of the chemical composition of the bio-oil in the different modes is presented in **Figure 19**. The in-situ experiments result in slightly higher acids and phenols yields, while the rest of the compounds were either reduced or not changed. Higher acids yield can also be attributed to the relative poor catalyst/vapor contact in the in-situ mode. For in-situ applications of the catalyst, a high catalyst/biomass ratio can compensate the poor catalyst/vapor contact. In the present work, the catalyst/biomass ratio could not further be increased due to practical operation limitations of the entrained down flow reactor system. However, in a commercial system like a fluidized bed, higher catalyst/biomass ratios can be implemented to improve the catalyst/vapor contact and to achieve a higher level of de-oxygenation.

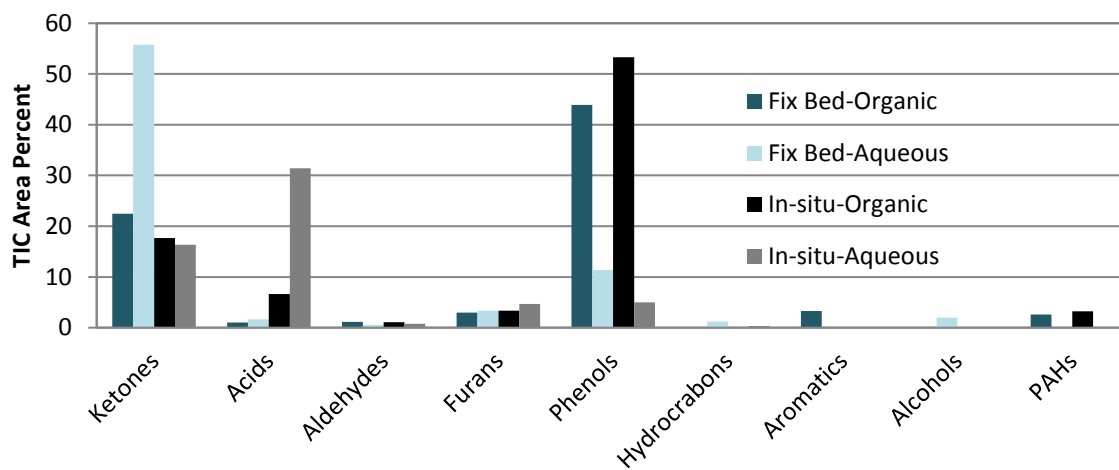
## 4.4 Conclusions

It is evident that  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  is a promising catalyst to improve the deleterious properties of the bio-oil. A high level of de-oxygenation was achieved using both experimental modes of operation, post treatment of pyrolysis vapor and in-situ upgrading of pyrolysis vapors. The catalytically produced bio-oil had a high calorific value and was rich in valuable chemical compounds. Acids in the bio-oil were completely removed resulting in a neutral pH bio-oil that can improve handling and stability characteristics of the bio-oil. Such a remarkable improvement in quality of bio-oil is of high significance

towards production of a green fuel precursor. This high energy bio-oil, rich in organics, with low water and oxygen content can be upgraded via hydrotreatment for fuel application.



**Figure 18:** a. Effect of catalytic pyrolysis mode on the yields of different products b. Effect of catalytic pyrolysis mode on the gas composition c. Effect of catalytic pyrolysis mode on the characteristics of organic fraction of the liquid



**Figure 19:** Effect of catalytic pyrolysis mode on the chemical composition of the liquid.

## 4.5 References

1. Bridgwater, A.V., *Catalysis in thermal biomass conversion*. Applied Catalysis A: General, 1994. **116**(1–2): p. 5-47.
2. Sharma, R.K. and N.N. Bakhshi, *Catalytic upgrading of biomass-derived oils to transportation fuels and chemicals*. The Canadian Journal of Chemical Engineering, 1991. **69**(5): p. 1071-1081.
3. Bridgwater, A.V. and M.L. Cottam, *Opportunities for biomass pyrolysis liquids production and upgrading*. Energy & Fuels, 1992. **6**(2): p. 113-120.
4. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. Biomass and Bioenergy, 2012. **38**(0): p. 68-94.
5. Maggi, R. and B. Delmon, *Characterization and upgrading of bio-oils produced by rapid thermal processing*. Biomass and Bioenergy, 1994. **7**(1–6): p. 245-249.
6. Pattiya, A., J.O. Titiloye, and A.V. Bridgwater, *Fast pyrolysis of cassava rhizome in the presence of catalysts*. Journal of Analytical and Applied Pyrolysis, 2008. **81**(1): p. 72-79.
7. Suzuki, T., H. Ohme, and Y. Watanabe, *Alkali metal catalyzed carbon dioxide gasification of carbon*. Energy & Fuels, 1992. **6**(4): p. 343-351.
8. Lee, S., et al., *The effect of Na<sub>2</sub>CO<sub>3</sub> on the catalytic gasification of rice straw over nickel catalysts supported on kieselguhr*. Korean Journal of Chemical Engineering, 2000. **17**(2): p. 174-178.
9. Di Blasi, C., C. Branca, and A. Galgano, *Effects of Diammonium Phosphate on the Yields and Composition of Products from Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2006. **46**(2): p. 430-438.
10. Di Blasi, C., C. Branca, and A. Galgano, *Thermal and catalytic decomposition of wood impregnated with sulfur- and phosphorus-containing ammonium salts*. Polymer Degradation and Stability, 2008. **93**(2): p. 335-346.
11. Di Blasi, C., A. Galgano, and C. Branca, *Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2009. **48**(7): p. 3359-3369.
12. Wang, J., et al., *Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass*. Thermochemica Acta, 2006. **444**(1): p. 110-114.
13. Bradbury, A.G.W., Y. Sakai, and F. Shafizadeh, *A kinetic model for pyrolysis of cellulose*. Journal of Applied Polymer Science, 1979. **23**(11): p. 3271-3280.
14. Demirbas, A., *Biorefineries: Current activities and future developments*. Energy Conversion and Management, 2009. **50**(11): p. 2782-2801.
15. Raveendran, K., A. Ganesh, and K.C. Khilar, *Influence of mineral matter on biomass pyrolysis characteristics*. Fuel, 1995. **74**(12): p. 1812-1822.
16. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
17. Sanna, A., et al., *Bio-oil and bio-char from low temperature pyrolysis of spent grains using activated alumina*. Bioresource Technology, 2011. **102**(22): p. 10695-10703.
18. Nguyen, T.S., et al., *Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts*. Bioresource Technology, 2013. **142**(0): p. 353-360.

19. Biagini, E., M. Cioni, and L. Tognotti, *Development and characterization of a lab-scale entrained flow reactor for testing biomass fuels*. Fuel, 2005. **84**(12–13): p. 1524-1534.
20. Brown, A.L., et al., *Design and Characterization of an Entrained Flow Reactor for the Study of Biomass Pyrolysis Chemistry at High Heating Rates*. Energy & Fuels, 2001. **15**(5): p. 1276-1285.
21. Demirbas, A., *Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues*. Journal of Analytical and Applied Pyrolysis, 2004. **72**(2): p. 243-248.
22. Huber, G.W., et al., *Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates*. Science, 2005. **308**(5727): p. 1446-1450.
23. Climent, M.J., et al., *Mesoporous Materials as Catalysts for the Production of Chemicals: Synthesis of Alkyl Glucosides on MCM-41*. Journal of Catalysis, 1999. **183**(1): p. 76-82.
24. Diebold, J.P., *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*. , N.R.E. Laboratory, Editor. 2000.
25. Xu, J., et al., *Rice husk bio-oil upgrading by means of phase separation and the production of esters from the water phase, and novolac resins from the insoluble phase*. Biomass and Bioenergy, 2010. **34**(7): p. 1059-1063.
26. Demirbas, A., *Hydrogen Production from Biomass via Supercritical Water Gasification*. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2010. **32**(14): p. 1342-1354.
27. Guo, Y., et al., *Review of catalytic supercritical water gasification for hydrogen production from biomass*. Renewable and Sustainable Energy Reviews, 2010. **14**(1): p. 334-343.

## CHAPTER 5:

# Catalytic flash pyrolysis of oil-impregnated-wood and jatropha cake using sodium-based catalysts<sup>12</sup>

**Abstract:** Catalytic pyrolysis of wood with impregnated vegetable oil was investigated and compared with catalytic pyrolysis of jatropha cake making use of sodium-based catalysts to produce a high quality bio-oil. The catalytic pyrolysis was carried out in two modes: in-situ catalytic pyrolysis and post treatment of the pyrolysis vapors. The in-situ catalytic pyrolysis was carried out in an entrained flow reactor system using a premixed feedstock of  $\text{Na}_2\text{CO}_3$  and biomass and post treatment of biomass pyrolysis vapor was conducted in a downstream fixed bed reactor of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ . Results have shown that both  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  can be used for the production of a high-quality bio-oil from catalytic pyrolysis of oil-impregnated-wood and jatropha cake. The catalytic bio-oil had very low oxygen content, water content as low as 1 wt.%, a neutral pH, and a high calorific value upto 41.8 MJ/kg. The bio-oil consisted of high value chemical compounds mainly hydrocarbons and undesired compounds in the bio-oil were either completely removed or considerably reduced. Increasing the triglycerides content (vegetable oil) in the wood enhanced the formation of hydrocarbons in the bio-oil. Post treatment of the pyrolysis vapor over a fixed bed of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  produced superior quality bio-oil compared to in-situ catalytic pyrolysis with  $\text{Na}_2\text{CO}_3$ . This high-quality bio-oil may be used as a precursor in a fractionating process for the production of alternative fuels.

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## 5.1 Introduction

Flash pyrolysis is a simple process to convert biomass into a liquid, gas and solid product, and it requires a simple and inexpensive construction [1]. The process is mainly focused on maximizing the yield of the liquid product. However, pyrolysis-oil (hereinafter "bio-oil") produced with current flash pyrolysis technologies is not suitable for direct use as a transportation fuel or fuel additive because it is very different from petroleum derived fuels. Bio-oil is very much similar to that of the original biomass with respect to the chemical composition and is composed of a very complex mixture of oxygenated hydrocarbons [2]. The main disadvantages of using bio-oil as a diesel fuel are the low heating value which is approximately 40% less than that of fuel oil, its high viscosity, and the substantial solids content [3]. As well, bio-oil typically contains up to 25 wt.% water that cannot be readily separated, this causes miscibility problems with conventional fuel oils and as a result blends cannot be achieved [3]. The bio-oil has been described as acidic, corrosive, polar, thermally unstable, and highly oxygenated [3-6]. The presence of oxygenated compounds in the bio-oil is considered main responsible for all its deleterious properties. Therefore, in order to improve the quality of the bio-oil, the oxygen needs to be removed and the large molecules derived from lignin need to be reformed into more useful products. Catalytic de-oxygenation is considered as a first line option to overcome the problematic characteristics of the bio-oil.

In the past, most of catalytic applications focused on post upgrading of the bio-oil e.g. via hydrotreatment of the bio-oil. [7-10]. Recently more interest is in catalytic pyrolysis of biomass since it eliminates costly condensation and re-evaporation procedures prior to the bio-oil upgrading. The catalytic pyrolysis studies mainly focused on zeolites and mesoporous aluminosilicates but the resulted bio-oil is still far from the desired qualities and especially failed to achieve any significant de-oxygenation of the bio-oil, and the product still requires expensive upgrading before it can be used as a fuel. Furthermore, relatively small pore zeolites resulted in significant decrease in organics yield due to the increase of the production of water and gases, and rapid catalyst deactivation occurs because of coke deposition [11]. This work is focused on developing a novel catalyst that can produce a high-quality bio-oil in a single integrated catalysis-pyrolysis reactor. Such a bio-oil can be directly used to produce fuels and chemicals using existing refining infrastructure.

The effect of alkali compounds and activated alumina on the properties of bio-oil has not studied systematically and there is very limited literature available for catalytic pyrolysis of biomass. Alkali metals are found to be effective catalysts for H<sub>2</sub>O and CO<sub>2</sub> gasification of carbon. Several researchers used alkali compounds as catalyst for biomass pyrolysis and found that alkali compounds lowered the temperatures of biomass de-volatilization and decreased biomass conversion time [12-16]. Alkali metals can be applied directly for catalytic biomass pyrolysis but direct addition of alkali metal catalysts has several disadvantages, e.g. difficult and expensive recovery of the catalyst. To solve these problems, alkali metal can be supported on a catalyst carrier e.g. alumina and taking advantage of catalytic effects of both alumina and the alkali metal. Very few studies could be found on active alumina as a solid acid catalyst for catalytic pyrolysis of biomass [17]. Compared to zeolites, alumina has larger pores, and this can reduce the coke formation and enhance the organic liquid yield due to its lower acidity. Larger molecules,



particularly lignin-derived compounds, can enter, reformulate and exit the bigger pores of alumina with lesser chances of coke formation and pore blockage.

A new catalyst is developed based on systematic studies with batch experiments on laboratory scale where  $\text{Na}_2\text{CO}_3$  was supported on  $\gamma\text{-Al}_2\text{O}_3$  and used for catalytic pyrolysis of biomass [18]. It is shown that  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  can produce a good quality bio-oil with low oxygen content, high calorific value and almost neutral in pH. However, the produced bio-oil has a low content of hydrocarbons and a high content of ketones and phenols, and needs extensive pretreatment to be used as a fuel. In the present work, we studied the effect of adding a small quantity of a triglycerides rich source like vegetable oil to the wood, to control the thermo-chemical reactions and producing a hydrocarbon-rich bio-oil. It is well known that triglyceride based vegetable oils or animal fats can be pyrolyzed to produce hydrocarbon rich liquid fuels [19], but due to limited availability of vegetable oil and waste oil/fats, they cannot fulfill the huge demand to alternative fuels. Co-pyrolysis of biomass with a minor amount of vegetable oil could be more feasible in case the resulting bio-oil has a superior quality to the conventional wood pyrolysis liquid. Information about the combined catalytic pyrolysis of wood and vegetable oil is not available in literature. Triglycerides (vegetable oil) have the advantage compared to lignocellulosic biomass of having a high energy and a low oxygen content [20]. The main focus of this work is to study the effect of sodium based catalysts and co-pyrolysis of wood and vegetable oil in order to produce a high value bio-oil that can be used for fuel applications.

As an alternative for the vegetable oil-impregnated-wood, a biomass feedstock like jatropha seed cake can be used. As jatropha seed cakes contain a substantial amount of residual triglycerides after the oil extraction process. After the proof-of-concept with vegetable oil-impregnated-wood, the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Na}_2\text{CO}_3$  is used for the catalytic pyrolysis of jatropha seed cake to produce a high-quality bio-oil enriched with hydrocarbons. The post treatment of vapors from jatropha cake and vegetable oil-impregnated-wood pyrolysis was carried out in a catalytic fixed bed reactor of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ , and the in-situ catalytic pyrolysis was conducted with a mixture of biomass and  $\text{Na}_2\text{CO}_3$  in an entrained flow reactor system.

## 5.2 Materials and Methods

Material and methods have been described in Chapter 4, section 4.2. Schematic presentation of the experimental setup in **Figure 14**. Other operating conditions and parameters are listed in **Table 8**.

The biomass used for the experiments consisted of wood fibres and is commercially available with the trade name LIGNOCEL by J. RETTENMAIER & SÖHNE GmbH. The de-oiled jatropha cake was obtained from a local Dutch supplier. The ultimate (wet basis) and proximate analyses of Lignocel, jatropha cake and sunflower vegetable oil (available over the counter for household) are presented in **Table 20**.

**Table 20:** Ultimate and proximate analysis of biomass feedstock (wet basis).

	C	H	N	O <sup>13</sup>	Moisture	Volatile	Fixed	Ash	LHV
	[%]	[%]	[%]	[%]	[%]	s	C.	[%]	[MJ/kg]
						[%]	[%]		
Lignocel	49.2	5.7	0.1	45.0	6.5	76.4	13.6	3.5	16.6
Jatropha Cake	46.9	7.1	4.7	41.3	4.8	74.5	16.4	4.3	18.8
Sunflower Oil	78.0	11.4	0.5	10.0	-	-	-	-	39.8

### 5.2.1 Catalysts

Na<sub>2</sub>CO<sub>3</sub> supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by wet impregnation of 10% and 20% of Na<sub>2</sub>CO<sub>3</sub> by weight. Na<sub>2</sub>CO<sub>3</sub> (ACS reagent grade >99.5%) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained from Sigma Aldrich and Albemarle respectively. A saturated solution of sodium carbonate was prepared at room temperature (21 g Na<sub>2</sub>CO<sub>3</sub> per liter of water) and heated to 60 °C. Alumina carrier ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was added to the Na<sub>2</sub>CO<sub>3</sub> solution and stirred for 2 hours keeping at 60 °C. After two hours, the catalyst was dried in an oven at 105 °C to evaporate the water. Finally, the catalyst was calcined in an oven at 600 °C for 12 hours and stored in a desiccator. Catalyst characterization has been described in detail by Nguyen et al. [18].

### 5.2.2 Product analysis

The non-condensable gases leaving the RPS mainly compose of carbon dioxide, carbon monoxide and C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> hydrocarbons. The volumetric flow rate of these gases is measured with a gas flow meter and a sample of this stream is pumped to an on-line gas analysis unit. Infrared analyzers are used to measure CO, CO<sub>2</sub> and an FID analyzer is used to measure hydrocarbons. The liquid is analysed with an elemental analyser to find out the elemental composition. The water contents of the oil are quantified by Karl Fisher titration, and a bomb calorimeter is used to determine the heating value of the bio-oil. An Agilent GC-MS is used to analyse the bio-oil and the NIST8 library is used to detect the components.

<sup>13</sup> by difference

## 5.3 Catalytic pyrolysis of vegetable oil-impregnated-wood

A series of preliminary experiments was conducted to optimise the pyrolysis reaction conditions in the entrained flow reactor for a maximum liquid yield. For non-catalytic pyrolysis experiments, denoted by Reference 1, the optimum conditions were established at 500 °C reactor temperature and 4 seconds residence time of biomass and vapors. The same operating conditions were used for the catalytic experiments in order to compare the effect of the catalyst on the composition and yield of the different pyrolysis products. About 15 wt.% of the vegetable oil was impregnated onto the wood. The vegetable oil was physically mixed with the wood and the mixture was left for 24 hours for good absorption of the vegetable oil in the wood and this mixture was used for non-catalytic pyrolysis experiment and denoted by Reference 2. This oil-impregnated-wood was used in experiments for post treatment of the pyrolysis vapors in a fixed bed reactor of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ . For the in-situ catalytic pyrolysis experiments with  $\text{Na}_2\text{CO}_3$ , the oil-impregnated-wood (preparation described in previous paragraph) was physically mixed with different concentrations of  $\text{Na}_2\text{CO}_3$ : 2%, 5% 10% and 20% of  $\text{Na}_2\text{CO}_3$  by weight.

### 5.3.1 In-situ catalytic pyrolysis with $\text{Na}_2\text{CO}_3$ in an entrained flow reactor system

The effect of the  $\text{Na}_2\text{CO}_3$  concentration was studied for in-situ catalytic pyrolysis and results have been compared with the non-catalytic experiments of wood (Reference 1 experiment) and with 15 wt.% oil-impregnated-wood (Reference 2 experiment). The product yields on basis of the feed (wood and 15 wt.% of vegetable oil) and the composition of the gas product (as the relative selectivity to  $\text{CO}$ ,  $\text{CO}_2$  and hydrocarbons) are presented in **Table 21**. In all experiments, a reasonable total mass balance was achieved. In contrast to wood pyrolysis (Reference 1 experiment), all oil-impregnated-wood pyrolysis experiments resulted in a phase separation of the liquid product. The liquid was instantaneously separated into an aqueous and an organic fraction in the condenser. This phase separation made it possible to separate the organic fraction from the aqueous fraction using a conical separation flask. For Reference 1 experiment, the water content of the liquid has been presented as the aqueous fraction but in practice there was no phase separation achieved.

Increasing the concentration of  $\text{Na}_2\text{CO}_3$  from 2% to 20% had a significant effect on the pyrolysis products. A higher  $\text{Na}_2\text{CO}_3$  concentration produced significantly more gas because of de-oxygenation and cracking of the pyrolysis vapors and this reduced the amount of liquid. The catalyst seemed to have no influence on the char yields. The char yield was corrected by subtracting the  $\text{Na}_2\text{CO}_3$  recovered with char. The type of gaseous products formed ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_x\text{H}_y$ ) indicates the extent of de-oxygenation:  $\text{Na}_2\text{CO}_3$  favored the ideal de-oxygenation route of de-carboxylation. Detailed analysis of the organic fraction of the pyrolysis liquid (bio-oil) is presented in **Table 22**. The Aqueous fraction of the liquid product mainly consisted of water and an elemental analysis was not reliable. The GC-MS analysis of aqueous fraction is discussed in section 3.4. The  $\text{Na}_2\text{CO}_3$  catalyst had a significant effect on the bio-oil properties and noticeable improvements in the bio-oil quality were achieved. The oxygen content of the bio-oil reduced from 25.5% (Reference 2) to 11.4% (10%  $\text{Na}_2\text{CO}_3$ ), a concentration of 5 wt.%  $\text{Na}_2\text{CO}_3$  is found to be optimum for a reasonable de-oxygenation of 16.1% oxygen and an a yield of 23.2 wt.%

of the bio-oil. A higher concentration than 5 wt.%  $\text{Na}_2\text{CO}_3$  caused a significant reduction in the bio-oil yield and a higher production of gas. The experimental results show that the  $\text{Na}_2\text{CO}_3$  catalyst has the desired effect on the properties of bio-oil. The application of  $\text{Na}_2\text{CO}_3$  resulted in a very high de-oxygenation of the bio-oil while the oxygen is mainly captured in the form of  $\text{CO}_2$ . This follows the ideal order of de-oxygenation i.e.  $\text{CO}_2 > \text{CO} > \text{C}_x\text{H}_y$  aimed at removing maximum oxygen with a single carbon atom and maximizing the hydrogen content in the bio-oil.

**Table 21:** Product yields weight % for non-catalytic and in-situ catalytic pyrolysis experiments in entrained flow reactor

	A.F. <sup>14</sup>	O.F. <sup>15</sup>	T.L. <sup>16</sup>	Gas	Char	$\text{CO}_2$	CO	$\text{C}_x\text{H}_y$	T.M. <sup>17</sup>
Reference 1 <sup>18</sup>	20.0	43.6	63.6	11.6	16.3	40.4	43.5	16.1	91.5
Reference 2 <sup>19</sup>	19.3	25.5	44.8	19.8	15.6	20.1	55.4	24.5	80.2
In-situ 2% $\text{Na}_2\text{CO}_3$	29.6	23.3	52.9	25.0	17.1	55.7	36.1	8.2	95
In-situ 5% $\text{Na}_2\text{CO}_3$	24.8	23.2	48	20.8	17.6	59.7	29.9	10.4	86.4
In-situ 10% $\text{Na}_2\text{CO}_3$	23.1	13.9	37	46.9	11.1	58.7	25.2	15.9	95
In-situ 20% $\text{Na}_2\text{CO}_3$	18.0	10.0	28	43.7	14.0	47.3	33.8	17.8	85.7

Experiments were performed to see the effect of varying the vegetable oil concentration in the wood on the bio-oil properties. Experiments were performed using 5 wt.%  $\text{Na}_2\text{CO}_3$  for 5 wt.% and 15 wt.% oil impregnated in wood and results are presented in **Figure 20a** and **Figure 20b**. **Figure 20a** shows that for 5 wt.% impregnations of oil in wood, the yield of the organic liquid fraction is 13.5 wt.%. This implies that the organic liquid product is mainly the product of wood conversion as the 5 wt.% impregnated oil can only contribute 3.5 wt.% to this organic fraction considering 70% conversion of vegetable oil to liquids. **Figure 20b** shows that lowering the vegetable oil concentration down to 5 wt.% had a negative impact on both the quality and yield of the bio-oil. The negative

<sup>14</sup> Aqueous Fraction of the Liquid

<sup>15</sup> Organic Fraction of the Liquid

<sup>16</sup> Total Liquid

<sup>17</sup> Total Mass Balance

<sup>18</sup> Non-catalytic experiments of wood only

<sup>19</sup> Non-catalytic experiments of oil-impregnated-wood

impact of lowering the vegetable oil concentration on the chemical composition of the bio-oil will be further discussed in section 3.3.2.

**Table 22:** Characteristics of organic fraction of the liquid (Bio-oil) obtained from non-catalytic and in-situ catalytic pyrolysis experiments in entrained flow reactor 20

	C	H	O	Water	HHV
	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
Reference 1	47.8	6.2	45.4	31.5	17.8
Reference 2	67.2	6.7	25.5	5.4	28.0
In-situ 2% Na <sub>2</sub> CO <sub>3</sub>	72.0	9.0	18.2	4.2	34.0
In-situ 5% Na <sub>2</sub> CO <sub>3</sub>	74.2	9.0	16.1	3.9	35.1
In-situ 10% Na <sub>2</sub> CO <sub>3</sub>	78.0	9.5	11.4	1.6	38.0
In-situ 20% Na <sub>2</sub> CO <sub>3</sub>	75.9	8.9	14.7	2.5	35.8

### 5.3.2 Post treatment of pyrolysis vapors over a fixed bed of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported Na<sub>2</sub>CO<sub>3</sub>

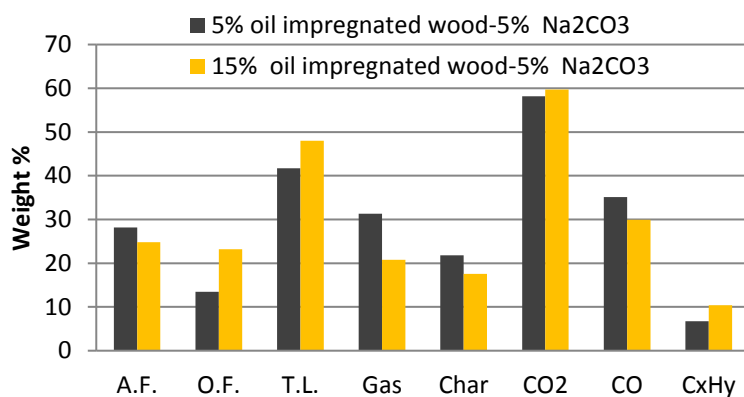
In the previous section, results have been presented for in-situ catalytic pyrolysis with a mixture of oi-impregnated-wood and Na<sub>2</sub>CO<sub>3</sub> in an entrained flow reactor system. The Na<sub>2</sub>CO<sub>3</sub> catalyst proved to have a positive effect on the properties of the bio-oil. In practical applications, the impregnation of Na<sub>2</sub>CO<sub>3</sub> onto the wood will not be techno-economic feasible, and recovery of the Na<sub>2</sub>CO<sub>3</sub> catalyst and corrosion/erosion problems by Na<sub>2</sub>CO<sub>3</sub> will pose technical challenges and operational obstacles. Another possible concern may be that traces of sodium will be present in the bio-oil, impeding its use. Supporting Na<sub>2</sub>CO<sub>3</sub> on a carrier like alumina may solve these problems. Alumina supported Na<sub>2</sub>CO<sub>3</sub> can be applied in a conventional reactor system e.g. a fluidized bed reactor or a cyclonic reactor system [21] by (partly) replacing the heat carrier (sand particles). The catalyst also needs to possess certain mechanical strength and stability as coke deposition requires a continuous regeneration of the catalyst. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is well known commercially available support and has proven the capacity to cope with these technical challenges in a continuous regeneration combustor [22]. The heat recovered from coke combustion can be utilized for the endothermic pyrolysis reaction.

In the present study Na<sub>2</sub>CO<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is applied in a fixed bed reactor to investigate its catalytic activity and to improve the catalyst/vapor contact compared to the case of in-situ catalytic pyrolysis. Two different Na<sub>2</sub>CO<sub>3</sub> concentrations (10% and 20 % by weight)

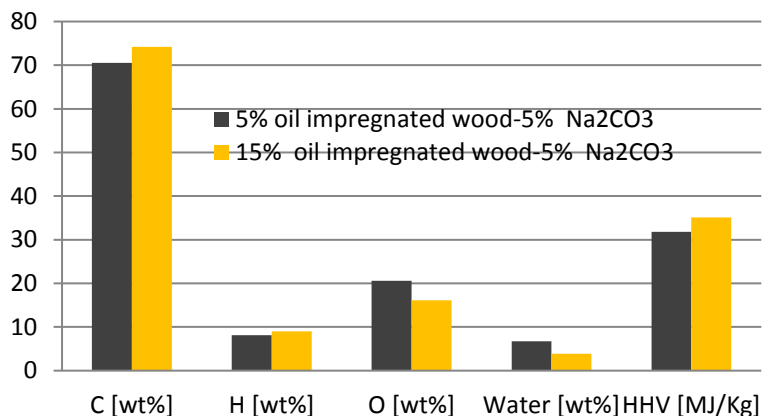
<sup>20</sup> The elemental composition and higher heating value of the bio-oil are presented on dry basis

were supported on alumina to study its effect on the bio-oil properties. The pyrolysis reactor temperature was fixed at 500 °C and the produced vapor/gas stream was passed over a fixed bed of 200 gram Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The temperature of the fixed bed reactor was also fixed at 500 °C for all the experiments. A catalyst/biomass ratio of 1:1 was used for the experiments by feeding a limited amount of 200 g of oil-impregnated-wood to the pyrolysis reactor. In a limited amount of time, a slight reduction in catalyst activity was observed due to coke formation at the catalyst when more than 200 g of biomass was fed in a single batch of experiment. The catalyst requires a continuous combustion of coke (regeneration) to maintain its activity that was not possible in current experimental scheme.

2a



2b



**Figure 20:** a. Effect of vegetable oil concentration on pyrolysis product yields weight % b. Effect of vegetable oil concentration on characteristics of the bio-oil.

The product yields and the bio-oil properties after catalytic post treatment are presented in **Table 23** and **Table 24**, respectively. The results show that post treatment of the pyrolysis vapors with the Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was able to produce an organic liquid with high calorific values and low oxygen contents. For example for 20% Na<sub>2</sub>CO<sub>3</sub> an organic liquid yield of 17.2% was obtained with an oxygen content of 9.9 wt.% and a

calorific value of 38.8 MJ/kg organic liquid. From the gas compositions, it can be seen that for the higher Na<sub>2</sub>CO<sub>3</sub> concentration (20%) de-carboxylation is favored over de-carbonylation, these results are in consistent with previous observation presented in Table 3. The catalytic conversion with Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> also led to the production of coke. Nguyen et al. has described that this coke has a high oxygen content up to 41.5 wt.% and the coke formation on the catalyst appears to be a major de-oxygenation route [18].

**Table 23:** Product yields weight % for post treatment of pyrolysis vapor over fixed bed of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

	A.F.	O.F.	T.L.	Gas	Char	Coke	CO <sub>2</sub>	CO	C <sub>x</sub> H <sub>y</sub>
10 % Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	22.1	13.3	35.4	30.3	14.3	9.1	48	36.1	14.9
20% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	16.2	17.2	33.4	40.2	15.2	8.9	62.3	22.8	14.7

**Table 24:** Characteristics of organic fraction of the liquid (Bio-oil) for post treatment of pyrolysis vapor over fixed bed of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

	C	H	O	Water	HHV
	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
10 % Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	78.0	9.4	11.5	1.6	37.9
20% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	79.4	9.8	9.9	1.0	38.8

Comparing post treatment in a fixed bed with in-situ catalytic pyrolysis (both with e.g. 20% Na<sub>2</sub>CO<sub>3</sub>) shows that upgrading via post treatment is far superior over in-situ catalytic pyrolysis. This can be explained by the much better vapor/catalyst contact in a fixed bed system compared to the contact between the separate particle of wood and Na<sub>2</sub>CO<sub>3</sub> for in-situ catalytic pyrolysis. Compared to Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is more favorable for de-carboxylation rout over de-carbonylation by removing oxygen with minimum loss of carbon, the enhanced de-carbonylation in presence of γ-Al<sub>2</sub>O<sub>3</sub> can be attributed to inherit catalytic activity of γ-Al<sub>2</sub>O<sub>3</sub>.

The in-situ application of Na<sub>2</sub>CO<sub>3</sub> yielded a relatively lower organic liquid mainly because of a longer residence time of the pyrolysis vapors in the entrained flow reactor (> 4 sec). This led to severe cracking of thermo-chemically formed bio-oil vapors at high temperatures and formation of coke on the catalyst and char particles. Many researchers reported that a short contact time between the catalyst and the bio-oil vapors is favorable to simultaneously increase the yield of the bio-oil and to reduce the yield of coke [23]. The vapor residence time in the fixed bed reactor is less than half a second that does not favors the extensive cracking of the bio-oil vapors. As was seen for in-situ catalytic pyrolysis in the previous section, a higher concentration of Na<sub>2</sub>CO<sub>3</sub> than 10% lowered the quality and yield of the bio-oil, while for post treatment a higher concentration of Na<sub>2</sub>CO<sub>3</sub> increased the quality and yield of the bio-oil, again it may be attributed to shorter



residence time in fixed bed reactor that requires higher  $\text{Na}_2\text{CO}_3$  concentrations for upgrading of bio-oil vapors.

Although a high-quality bio-oil was achieved for post treatment over a fixed bed of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ , it is noted that a catalytic fixed bed in a pyrolysis system is not a favorable choice for practical applications. The main disadvantage of a catalytic fixed bed reactor is the difficulties in scaling-up and the regeneration of the catalyst. The entrained flow reactor is also not the favorite for catalytic pyrolysis because of the poor vapor/catalyst contact and the undesired long vapor residence time at high temperatures and in a coke/char environment. A fluid catalytic cracking (FCC) type process in a fluidized bed reactor could provide a much better solution for the continuous catalytic production of high quality biofuels and the regeneration of coked  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  [24]. Although being currently under investigation, the cyclonic PyRos reactor [21] can provide substantial advantages of a very short vapor residence time (less than half a second) over existing reactor systems for catalytic biomass pyrolysis, and can considerably improve the liquid yields and properties by avoiding excessive secondary cracking and contact of vapors with coke and char.

### 5.3.3 Post-regeneration activity of $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$

Catalyst regeneration is an important aspect to be considered for commercial applications. Normally a commercial catalyst is expected to retain its activity for a long time. To study the regenerated catalyst activity, the deposited coke on the catalyst was combusted in an oven for 12 hours and the thus regenerated catalyst was used again for experiments. The results for fresh and regenerated catalyst are presented in **Table 25** and **Table 26**. The regenerated catalyst produced less gas and resulted in a higher liquid yield compared to the fresh catalyst although the organic fraction was slightly altered. The regenerated catalyst produced more CO and hydrocarbon gases than  $\text{CO}_2$  and favored the de-carboxylation route and secondary cracking of pyrolysis vapors over de-carboxylation, this resulted in a bio-oil with a higher oxygen content, lower carbon and hydrogen content compared to the oil of a fresh catalyst

**Table 25:** Comparison of product yields (weight %) obtained with catalytic pyrolysis over fixed bed of fresh and regenerated  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$

	A.F.	O.F.	Gas	Char	Coke	$\text{CO}_2$	CO	$\text{C}_x\text{H}_y$
Fresh-20% Catalyst	16.2	17.2	33.4	40.2	15.2	8.9	62.3	22.8
Regenerated-20% Catalyst	30.7	15.9	26.0	15.7	5.6	13.5	67.4	19.0

A relative poor de-oxygenation of the regenerated catalyst can be attributed to a loss in catalyst activity because of the batch mode of the catalyst in the fixed bed. When the catalyst is employed for conversion of the bio-oil vapors without continuous regeneration, the catalyst pores may get partially blocked and show irreversible deactivation. After a while the pyrolysis vapors cannot enter the blocked catalyst pores and leave the reaction



zone without any reformation. In a commercial application, the catalyst will be employed with an efficient and continuous regeneration system and deactivation of the catalyst is not likely to happen. If we take the example of a FCC process, the small pores zeolites are successfully regenerated without loss of their catalytic activity. Alumina having even larger pore size is likely to show even better performance in an FCC kind of process for treatment of bio-oil vapors.

**Table 26:** Comparison of organic fraction (bio-oil) characteristics obtained with catalytic pyrolysis over fixed bed of fresh and regenerated Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

	C	H	O	Water	HHV
	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
Fresh-20% Catalyst	79.4	9.8	9.9	1.0	38.8
Regenerated-20% Catalyst	77.0	9.0	13.2	1.9	36.4

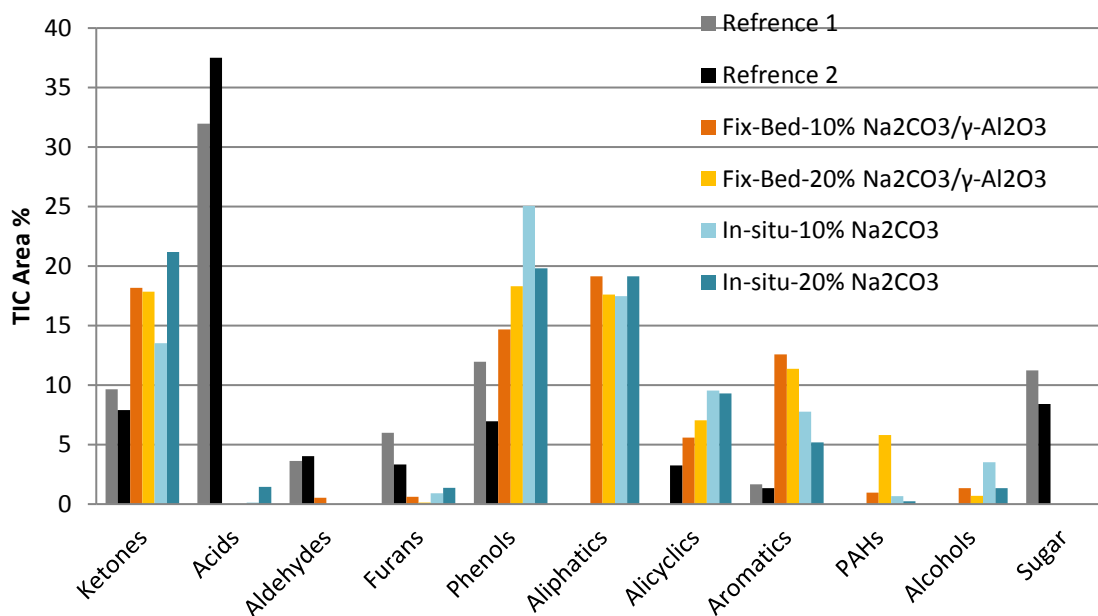
### 5.3.4 Bio-oil Characterization

The bio-oil obtained from the catalytic and non-catalytic pyrolysis was analyzed by GC-MS. As explained earlier the whole liquid fraction was used for non-catalytic wood pyrolysis (Reference 1 experiment) and the separated organic fraction (bio-oil) was used for oil-impregnated-wood pyrolysis (Reference 2 and catalytic experiments). A wide range of organic compounds are found in the bio-oil. The identified compounds of the organic phase are typically grouped as hydrocarbons, phenols, furans, carboxylic acids, alcohols, aldehydes, ketones, aromatics and PAHs (polycyclic aromatic hydrocarbons). In **Figure 21**, the chemical composition of bio-oil has been described as total ion chromatogram area percentages of all the compounds and the compounds have been classified according to their chemical nature.

Large amounts of desired compound are produced including aliphatic, alicyclic and aromatic liquid hydrocarbons using the two catalysts, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Hydrocarbons have high value for fuel industry. Both catalysts, resulted in a complete conversion of acids, aldehydes, sugars and significant reduction in furans, all these compounds are undesired as they impart deleterious properties to the bio-oil. Both catalysts caused substantial enhancement in the production of ketones and phenols, phenols and their alkylated derivatives are useful for the chemical industry.

Hydrocarbons (HCs) have the highest value for fuel applications and are considered as the most desired compounds in the bio-oil because of their high heating value. HCs are scarce in non-catalytic bio-oil, but the catalytic pyrolysis (with Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) has significantly increased the formation of HCs (including aliphatic, alicyclic and aromatic liquid hydrocarbons) to 37% TIC area and this resulted in a high energy bio-oil with a calorific value upto 38.8 MJ/kg. Huber et al., 2006a described three possible routes for the formation of HCs in biomass pyrolysis: (1) de-carboxylation, de-carbonylation and oligomerization of dehydrated products of sugars, *i.e.* furans into aromatic hydrocarbons,

(2) de-carboxylation of carboxylic acids into aliphatic hydrocarbons and CO<sub>2</sub> and (3) hydrogenation/hydrogenolysis of phenols into aromatic hydrocarbons. As both acids and sugars have been completely removed and the content of phenols has increased in the catalytic bio-oil compared to the non-catalytic one, this suggests that route 1 and 2 contribute more to the production of hydrocarbons in the bio-oil than route 3. Moreover, since the aliphatic hydrocarbons are the dominant among all HCs, it can be concluded that acids are the main precursor for HCs in our study. The gas composition also supports this hypothesis as CO<sub>2</sub> is the dominant component among the gaseous products.



**Figure 21:** Chemical composition of organic fraction of the liquid (bio-oil) obtained by non-catalytic and catalytic pyrolysis of oil-impregnated-wood

Acids are the most dominating compounds in the non-catalytic bio-oil and the applied catalysts completely removed the acids from the bio-oil. This is the most significant improvement in the quality of bio-oil as acids are the main contributor for acidity of the bio-oil [25]. Removal of acids will lower the corrosivity, will increase the pH and the stability, the calorific value and the handling properties of the bio-oil. Sugars being another contributor to the acidity of the bio-oil are completely removed in the catalytic bio-oil. Removal of these two major contributors (acids and sugars) to the acidity of bio-oil is clearly reflected in the acid measurements of the bio-oil as presented in **Table 27**. The tablecatalytic bio-oil is almost neutral in pH. Both catalysts caused complete conversion of aldehydes and a significant reduction in furans. The reduction of aldehydes is good for the stability and the shelf-life of the bio-oil.

Both catalysts produced high amounts of phenols, a high value compound especially for resin and adhesive industry making the process economically attractive. Phenols are lignin derived product made by the cracking of the phenyl-propane units of the macromolecule lattice [25]. Huber et al. suggested that the aromatics, phenols and their alkyl substituted

fractions are formed by recombination and cyclization reactions, via condensation from C2, C3 and C4 fragments which are the initial degradation product. A noticeable effect was the increased formation of ketones in presence of the sodium based catalysts. Ketones undergo condensation reactions and cause formation of higher molecular weight components by polymerization reactions and increase viscosity [26]. Formation of ketones in presence of catalyst poses a challenge for the stability of the bio-oil. Ketones can be upgraded via a post-hydrogenation step to obtain liquid alkanes as described by Huber et al. [27], this process involves aldol condensation and hydrogenation of ketones. Nevertheless, an increased ketones yield can be tolerated comparing the other benefits obtained in the presence of the catalyst such as complete removal of acids and aldehydes, significant reduction in the furans, high yield of hydrocarbons, contributing to a high calorific value and a high level of de-oxygenation.

**Table 27:** Acidity of bio-oil from pyrolysis of oil-impregnated-wood

	Reference 1	Reference 2	20% Na <sub>2</sub> CO <sub>3</sub>	20% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>
TAN <sup>21</sup>	159	172	7.63	4.16
pH	2.2-2.4	2.8	5.8	6.5

### 5.3.5 Effect of catalyst and reactor system on the chemical composition of the organic liquid

Comparing the chemical composition of bio-oil (presented in **Figure 21**) also shows the superiority of the Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> in fixed bed system over in-situ catalytic pyrolysis with Na<sub>2</sub>CO<sub>3</sub>. Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> formed less phenol and more HCs with selectivity to aromatics and PAHs. A higher conversion to aromatic hydrocarbons over Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> can be attributed to the larger pores of alumina that allow bigger molecules to enter its pores and reform into more useful products. The PAHs and aromatic compounds in the bio-oil are considered lignin derived products mainly by the decomposition of polysaccharides. Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> formed more PAHs, mainly naphthalenes and substituted naphthalenes while all fractions of aromatic compounds increased in the presence of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. It seems that Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> stimulated the catalytic reactions that favor the formation of PAHs such as cyclization, aromatization, condensation. Furthermore, alumina pores are large enough so that naphthalene and substituted naphthalenes can leave the pores after their formation before the polymerization of these products happens and cause coke formation. The large regular pores of alumina allow the diffusion of reactants in the catalyst and diffusion of the products out of catalyst, minimizing consecutive decomposition reactions [28]. The large pores of γ-Al<sub>2</sub>O<sub>3</sub> allow more molecules to enter the catalyst and experience the cracking and reforming reactions and their subsequent

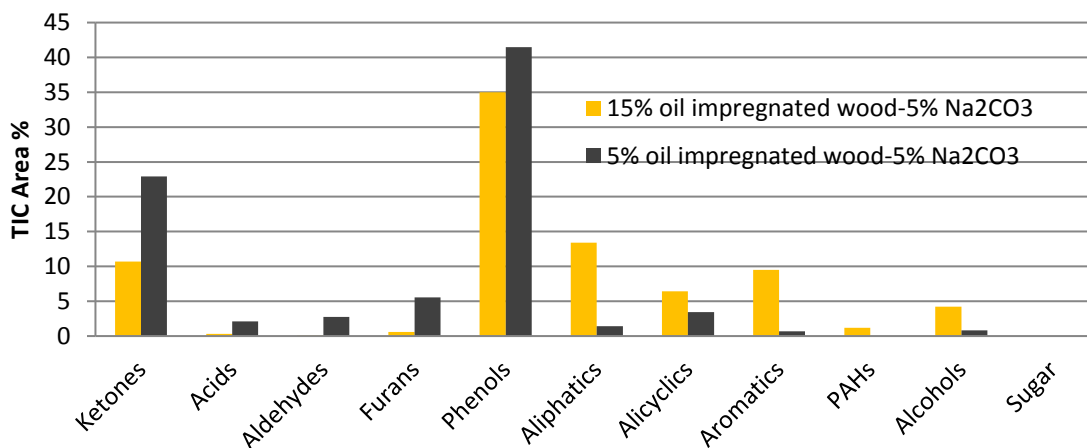
<sup>21</sup> Total acid number of bio-oil based on standard ASTM 664

aromatization. It seems that the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  is able to catalyze reactions that can convert oxygenated compounds into aromatic hydrocarbons such as de-carboxylation, de-carbonylation, de-hydration and aromatization.

The  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalytic system completely removed the acids, while for the  $\text{Na}_2\text{CO}_3$  catalyst a small amount of acids is found in the bio-oil, which can also be attributed to the relative poor catalyst/vapor contact for in-situ mode. In-situ catalytic pyrolysis with  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  can also pose poor catalyst/vapor contact problem, but a higher catalyst/biomass ratio can be implemented to improve the catalyst/vapor contact in a commercial system like a fluidized bed (FCC type).

### 5.3.6 Effect of the vegetable oil concentration on the chemical composition of the organic liquid

It is interesting to compare the chemical composition of the bio-oil from the experiments with 5 wt.% of vegetable oil and 15 wt.% vegetable oil (see **Figure 22**). For both experiments the catalyst effect is very similar for acids and sugars. The almost complete conversion of both acids and sugars proves that changing the vegetable oil concentration does not have any effect on these compounds. Lowering the vegetable oil considerably reduced the production of HCs while it increased the yields of phenols and ketones. Higher yields of HCs obtained using 15 wt.% vegetable oil could be attributed to the conversion of phenols to HCs due to the hydrogenation/hydrogenolysis of phenols as described by Huber et al. [29]. Possibly the lack of triglycerides also caused the reduced conversion of ketones to HCs.

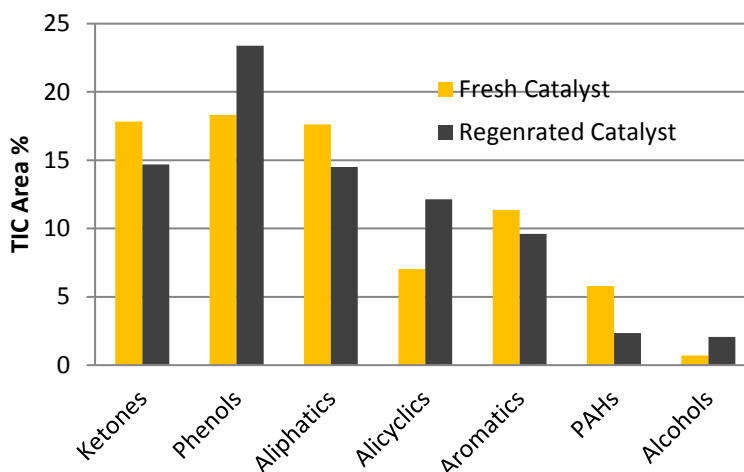


**Figure 22:** Effect of vegetable oil concentration on chemical composition of the bio-oil.

### 5.3.7 Effect of catalyst regeneration on the chemical composition of the organic liquid

**Figure 23** shows the effect of the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalyst regeneration on the bio-oil properties. There was not a big difference in activity of the fresh and regenerated catalysts. Both were able to remove the most undesirable compounds in the bio-oil,

including acids, aldehydes and furans, and they completely converted the sugars. The regenerated catalyst shows a slight different activity compared to that of the fresh catalyst regarding desired and valuable compounds of the bio-oil. It produced less ketones, aromatic, and aliphatic, and more phenols and alicyclic hydrocarbons. The reduced yields of PAHs can also be attributed to partial blocking of alumina pores.



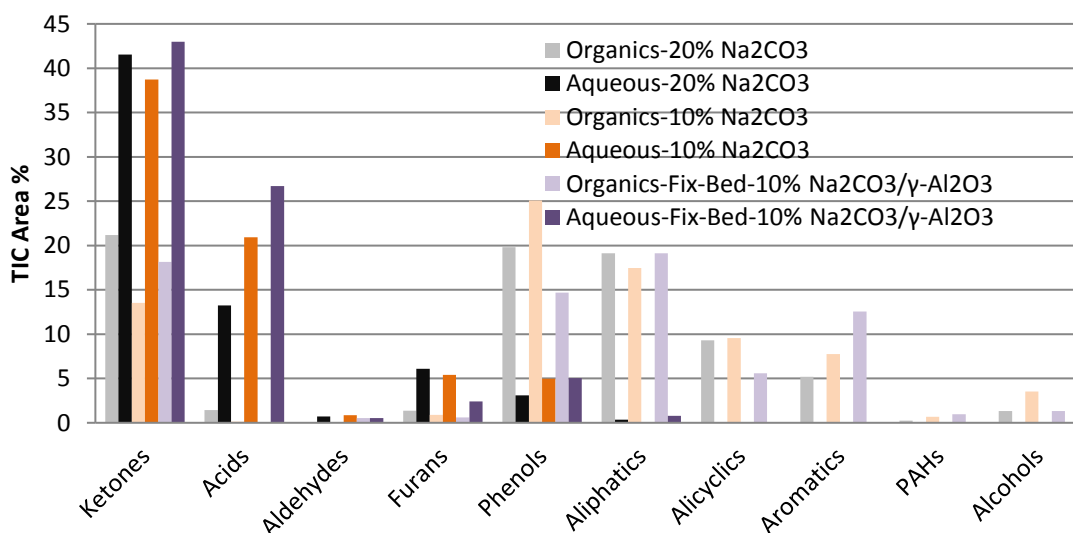
**Figure 23:** Effect of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  regeneration on chemical composition of the bio-oil.

### 5.3.8 Characterization of the aqueous fraction of the bio-oil

The aqueous fraction of the liquid obtained in the catalytic pyrolysis of biomass was analyzed for its water content and chemical composition. The aqueous fraction obtained in the catalytic experiments contained up to 90.6% water (see **Table 28**) and the rest were organics. Due to the high water content of the aqueous fraction, the elemental composition cannot accurately be obtained. The organics present in the aqueous fraction are analyzed by GC-MS and compared with the organics in the bio-oil (so called organic fraction of the pyrolysis liquid) in **Figure 24**. The desired compounds are scarce in the aqueous fraction while the undesired compounds and the phenols are abundant. The ketones yield is much higher in the aqueous fraction and lower in the organic fraction while the phenols fraction is significantly lower in the aqueous fraction than in the organic fraction. The highly polarity ketones are originated from the cellulose and hemicellulose components of the biomass and the phenolic compounds originates from the lignin fraction [30]. Acids and furans are also present in aqueous fraction. The aqueous fraction with a small portion of organics could be interesting for extraction and supercritical water gasification to produce hydrogen for hydrotreatment of the bio-oil [31, 32].

**Table 28:** Water content of aqueous fraction of liquid from catalytic pyrolysis of oil-impregnated-wood

Experiment	Water content [wt.%]
In-situ 2% Na <sub>2</sub> CO <sub>3</sub>	55.8
In-situ 5% Na <sub>2</sub> CO <sub>3</sub>	71.33
In-situ 10% Na <sub>2</sub> CO <sub>3</sub>	89.4
In-situ 20% Na <sub>2</sub> CO <sub>3</sub>	88.3
Fix-bed 10% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	87.6
Fix-bed 20% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	90.6

**Figure 24:** Chemical composition of organic and aqueous liquid fractions produced by catalytic pyrolysis of oil-impregnated-wood.

## 5.4 Catalytic flash pyrolysis of jatropha seed cake

Catalytic flash pyrolysis of vegetable oil-impregnated-wood with Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> has shown that hydrocarbon-rich bio-oil can be obtained from biomass in the presence of triglycerides. A biomass source that contains triglycerides can be a practical alternative to vegetable oil-impregnated-wood and jatropha seed de-oiled cake is a potential candidate that has a substantial amount of residual triglycerides after oil extraction process. Jatropha is considered as a potential biofuel source because of its rapid growth, easy propagation, higher oil content [33], small gestation period, wide range of environmental adaptation, and simple technology required for cultivation [34]. Catalytic pyrolysis of jatropha seed cake was performed for both in-situ catalytic pyrolysis with

Na<sub>2</sub>CO<sub>3</sub> in an entrained flow reactor and post treatment of pyrolysis vapors over the fixed bed of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. For in-situ catalytic pyrolysis with Na<sub>2</sub>CO<sub>3</sub>, a physically mixed feedstock of jatropha seed cake and Na<sub>2</sub>CO<sub>3</sub> (20 wt.%) was prepared. A batch of 200 gram of 20% Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> was used for the post treatment of pyrolysis vapors in a fixed bed catalyst system. A reference experiment was conducted for non-catalytic pyrolysis of jatropha seed cake. As for the non-catalytic pyrolysis experiments, the targeted maximum liquid yield was obtained at 500 °C reactor temperature and 4 seconds residence time of biomass/vapors in the pyrolysis reactor. Therefore, the same operating conditions were used for the catalytic experiments in order to be able to compare the effect of the catalyst on the nature and yield of the different products of jatropha cake pyrolysis. The temperature of the fixed bed reactor was also fixed at 500 °C for all the experiments. The liquid obtained had an instantaneous phase separation of an organic (bio-oil) and aqueous fraction. Being the fraction of interest, the organic liquid will be discussed in detailed. The product yields on basis of the wet initial weight of the jatropha cake are presented in **Table 29** and the bio-oil characteristics are presented in It is noted that the catalyst had a significant effect on the pyrolysis of jatropha seed cake. A high quality bio-oil was obtained by catalytic pyrolysis of jatropha seed cake using either Na<sub>2</sub>CO<sub>3</sub> for in-situ application or Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> in the fixed bed mode. Similar to oil-impregnated-wood, bio-oil upgrading of jatropha cake was superior in catalyst fixed bed of Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. Again this advantage can be attributed to the good vapor/catalyst contact in the fixed bed reactor and the additional catalytic activity of the alumina carrier. The in-situ application of Na<sub>2</sub>CO<sub>3</sub> yielded a relatively low organic liquid mainly because of the long residence time of the pyrolysis vapors in the entrained flow reactor (> 4 sec) and this led to severe cracking of the thermo-chemically formed pyrolysis vapors. On the other hand, the short vapor residence time in the fixed bed reactor prevents severe secondary cracking of the pyrolysis vapors. The combined activity of Na<sub>2</sub>CO<sub>3</sub> and alumina also favored de-carboxylation compared to de-carbonylation. As described in previous sections, the Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalytic system also exhibits de-oxygenation via the formation of coke. The high de-oxygenation via gas and coke formation resulted in an almost oxygen free bio-oil enriched in carbon and hydrogen.

**Table 30.** Due to the high-water content of the aqueous fraction (see **Table 31**), only the chemical composition can be characterized by the GC-MS.

**Table 29:** Product yields weight % for non-catalytic and catalytic pyrolysis of jatropha cake

	A.F.	O.F.	T.L	Gas	Char	Coke	CO <sub>2</sub>	CO	C <sub>x</sub> H <sub>y</sub>
Non-catalytic	11.5	23.0	34.5	5.8	22.7	N/A	62.6	18.9	18.5
In-situ Na <sub>2</sub> CO <sub>3</sub>	17.2	4.9	22.1	13.6	26.3	N/A	37.9	22.4	39.6
Fix-Bed Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	20.6	7.1	27.7	22.8	26.6	8.9	68.2	17.9	13.9

It is noted that the catalyst had a significant effect on the pyrolysis of jatropha seed cake. A high quality bio-oil was obtained by catalytic pyrolysis of jatropha seed cake using either Na<sub>2</sub>CO<sub>3</sub> for in-situ application or Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> in the fixed bed mode. Similar to oil-

impregnated-wood, bio-oil upgrading of jatropha cake was superior in catalyst fixed bed of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ . Again this advantage can be attributed to the good vapor/catalyst contact in the fixed bed reactor and the additional catalytic activity of the alumina carrier. The in-situ application of  $\text{Na}_2\text{CO}_3$  yielded a relatively low organic liquid mainly because of the long residence time of the pyrolysis vapors in the entrained flow reactor (> 4 sec) and this led to severe cracking of the thermo-chemically formed pyrolysis vapors. On the other hand, the short vapor residence time in the fixed bed reactor prevents severe secondary cracking of the pyrolysis vapors. The combined activity of  $\text{Na}_2\text{CO}_3$  and alumina also favored de-carboxylation compared to de-carbonylation. As described in previous sections, the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalytic system also exhibits de-oxygenation via the formation of coke. The high de-oxygenation via gas and coke formation resulted in an almost oxygen free bio-oil enriched in carbon and hydrogen.

**Table 30:** Characteristics of organic fraction of the liquid (bio-oil) for non-catalytic and catalytic pyrolysis of jatropha cake

	C	H	N	O	Water	HHV
	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[wt.%]	[MJ/Kg]
Non-catalytic	56.0	6.9	5.3	20.9	11.0	26.9
In-situ $\text{Na}_2\text{CO}_3$	75.9	9.5	7.5	7.1	6.8	36.7
Fix-Bed $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$	83.6	10.2	5.5	0.7	7.8	41.8

In **Figure 25**, the chemical composition of the pyrolysis liquid obtained from the catalytic and non-catalytic pyrolysis of jatropha cake has been described as total ion chromatogram area percentages and the identified compounds of the organic phase (bio-oil) and aqueous phase has been classified according to their chemical nature. A significant amount of undesired compounds including acids, aldehydes and furans as found in the Reference (non-catalytic) bio-oil were completely converted using the sodium based catalysts, and a large amount of hydrocarbons (mainly aliphatic HCs) were formed. The application of the catalysts also caused a reduction in the yields of ketone and phenols. As already mentioned in the experimental section, the nitrogen content of the jatropha seed cake is as high as 4.7%, and this is reflected in the bio-oil as N-compounds. N-compounds were also converted to some extent by the catalyst. The aqueous phase had very high water content and was very low in organics as shown in **Table 31**. It mainly consisted of undesired and N-compounds.

**Table 31:** Water content of aqueous fraction of liquid from non-catalytic and catalytic pyrolysis of jatropha cake

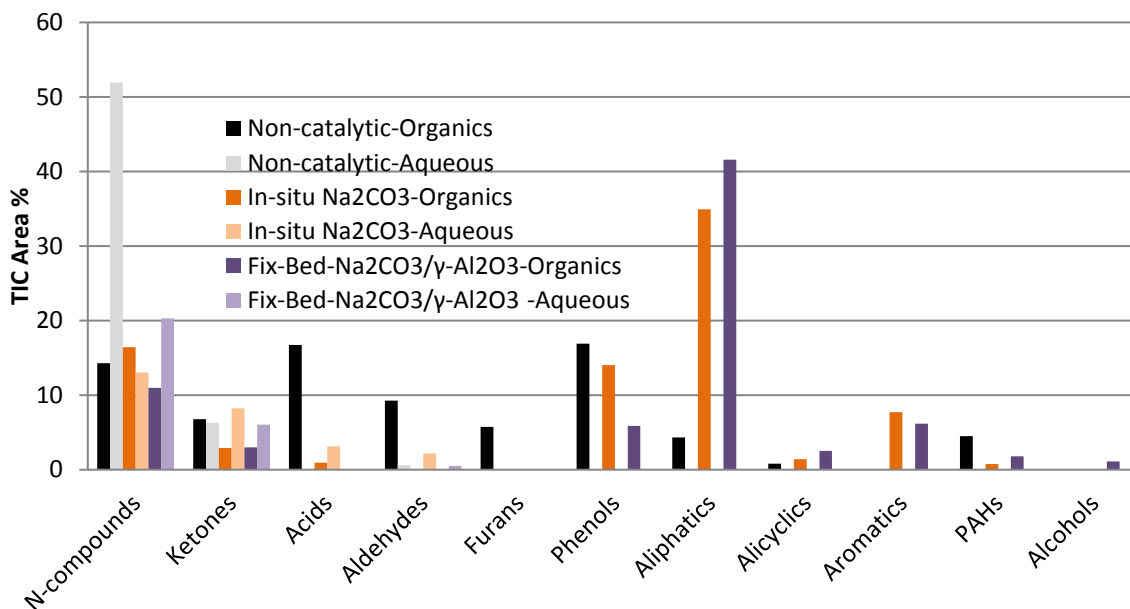
Experiment	Water content [wt.%]
Non-catalytic-Aqueous	82.98



In-situ Na<sub>2</sub>CO<sub>3</sub>-Aqueous 89.00

Fix-Bed- Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>-Aqueous 87.3

Chemical properties of the bio-oil produced with the Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> in the fix-bed mode are superior to that produced via in-situ catalytic pyrolysis with Na<sub>2</sub>CO<sub>3</sub>. A very high yield of aliphatic HCs was obtained with Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> i.e. 41.6%, while the formation of phenols, ketones and N-compounds was reduced. Compared to in-situ catalytic pyrolysis with Na<sub>2</sub>CO<sub>3</sub>, the increase in hydrocarbon selectivity and decrease in selectivity to phenols, ketones and N-compounds can be explained by the acidity and pore structure of the γ-Al<sub>2</sub>O<sub>3</sub> and the good catalyst/vapor contact in the fixed bed reactor.



**Figure 25:** Chemical composition of organic and aqueous liquid fractions of non-catalytic and catalytic pyrolysis of jatropha cake

Acid measurements of the bio-oil are presented in **Table 32**. The catalytic bio-oil produced in the fixed bed mode needs only 1.06 mg of KOH to titrate compared to 72.3 mg for non-catalytic bio-oil per 100 g of oil. The TAN measurement correlates well with the result of the elemental and chemical composition of the bio-oil. The thus produced non-acidic bio-oil will considerably improve storage and handling.

**Table 32:** Acidity of bio-oil from non-catalytic and catalytic pyrolysis of jatropha cake

	Non-catalytic	20% Na <sub>2</sub> CO <sub>3</sub>	20% Na <sub>2</sub> CO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub>
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TAN <sup>22</sup>	72.3	3.87	1.06
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The catalytic oil from jatropha cake with a high concentration of hydrocarbons, a low oxygen content and a high calorific value, can be an excellent precursor for a conventional fractioning process. In this way gasoline, diesel fuel or alternative fractional products to fuel-oils can be obtained. These fractions may either be used directly or by mixing with other conventional fuels. Bio-oil with its very low sulphur content may be an alternative for fuel-oil from the environmental pollution point of view. There are a number of alternative/substitutes to jatropha seed cake available, and these can be used, depending on the regional/local feasibility, to produce high quality biofuels via catalytic pyrolysis with Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.

## 5.5 Outlook

The current study has shown that a high value fuel precursor can be produced via catalytic pyrolysis of oil-impregnated-wood and jatropha cake. The key properties of catalytic bio-oil and fuel oils are compared in **Table 33**. Bio-oil produced via post treatment of (20% Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) of vapors from the pyrolysis of jatropha cake or 15 wt.% vegetable oil-impregnated-wood, is very similar to conventional fuel oil. Due to the limited supply of vegetable oil waste oil or fats, neither the vegetable oil can fulfill the huge demand to supplement for fuels, nor is the fuel production from vegetable oil economically feasible as they have a high value in the edible oil market [35]. But this study has shown that vegetable oils can be used as a minor supplement to the conventional biomass to produce a high quality bio-oil making the wood pyrolysis feasible both economically and technically. Process economics could be further improved by using lower value oils such as waste cooking or industrial oil.

As biofuels are more expensive than petroleum fuels, the economics for biomass pyrolysis are generally considered to be most favorable for plants which grow abundantly and require little cultivation in arid lands or industrial and agricultural wastes [36]. This work has shown that de-oiled seed cake from jatropha can be used as an alternative resource for the production of high quality bio-oil. The Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalytic system can be successfully implemented for catalytic pyrolysis of oil-impregnated-wood and jatropha seed cake to produce a high quality fuel precursor in a single conversion process. This fuel precursor has a neutral pH, contains no or very less water, is rich in hydrocarbons, having a high calorific value and contains very few oxygenated compounds. Furthermore, as the pyrolysis liquid shows indigenous separation of water, an almost water free bio-oil can solve the miscibility problem with conventional fuels.

The very low organic liquid yields obtained in the presence of the catalyst cannot be avoided if a high de-oxygenation of the bio-oil is required. This is caused by the loss of carbon and hydrogen associated with all routes of catalytic de-oxygenation. The catalyst properties and process parameters may be further optimized to increase the bio-oil yield. The amount of Na<sub>2</sub>CO<sub>3</sub> impregnated on the γ-Al<sub>2</sub>O<sub>3</sub> also needs further optimization to

<sup>22</sup> Total acid number of bio-oil based on standard ASTM 664

maximize the de-carboxylation reaction and to suppress the de-hydration and de-carbonylation reactions. The optimum type of catalytic pyrolysis reactor should have a long solid residence time for good conversion of the biomass and a short residence time for the vapors to avoid excessive secondary cracking and vapor contact with char and coke particle that can lead to unwanted gas and water formation. An integrated heat recovery from combustible gases, char and coke can increase the overall process efficiency and economics.

**Table 33:** Characteristics of Fuel-Oil and Bio-oil obtained from catalytic pyrolysis of oil-impregnated wood and jatropa cake.

Characteristics	oil-impregnated-wood bio-oil	Jatropha cake bio-oil	Fuel oil <sup>23</sup>
Water content (wt.%)	1.0	7.8	0.1
C (wt.%, dry)	79.4	83.6	85.3
H (wt.%, dry)	9.8	10.2	11.5
O (wt.%, dry)	9.9	0.7	1.0
HHV (MJ kg <sup>-1</sup> )	38.8	41.8	40
Acidity as mg of KOH/gm	4.16	1.06	0.2

## 5.6 Conclusion

Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> have shown to improve the quality of bio-oil for in-situ catalytic pyrolysis and for post treatment of pyrolysis vapors, respectively. Catalytically produced bio-oil from pyrolysis of vegetable oil-impregnated-wood and jatropa cake has very low oxygen content, water content as low as 1 wt.%, a neutral pH, and a high calorific value that is very close to that of fossil fuels. The catalytic bio-oil consists of high value chemical compounds for fuel application such as hydrocarbons. The incorporation of triglycerides

<sup>23</sup> 37. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.

in wood enhances the formation of hydrocarbons. Due to technical challenges associated with use of  $\text{Na}_2\text{CO}_3$  and due to comparative poor performance of  $\text{Na}_2\text{CO}_3$ , the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalytic system could be a first choice for commercial production of bio-oil. A high quality bio-oil can be produced in a single step of catalysis-pyrolysis eliminating the need for condensation and re-evaporation of bio-oil.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  also showed a good catalytic activity after regeneration. Neutral pH and absence of aldehydes will improve both handling and stability characteristics of the bio-oil. Hydrocarbons enriched bio-oil can be an attractive precursor for refining to produce alternative fuels.

## Triglycerides



### Chemical Structure



## 5.7 References

1. Onay, O. and O. Mete Koçkar, *Fixed-bed pyrolysis of rapeseed (Brassica napus L.)*. Biomass and Bioenergy, 2004. **26**(3): p. 289-299.
2. Bridgwater, A.V., *Review of fast pyrolysis of biomass and product upgrading*. Biomass and Bioenergy, 2012. **38**(0): p. 68-94.
3. Bridgwater, A.V., *Renewable fuels and chemicals by thermal processing of biomass*. Chemical Engineering Journal, 2003. **91**(2-3): p. 87-102.
4. Bridgwater, A.V. and G.V.C. Peacocke, *Fast pyrolysis processes for biomass*. Renewable and Sustainable Energy Reviews, 2000. **4**(1): p. 1-73.
5. Yaman, S., *Pyrolysis of biomass to produce fuels and chemical feedstocks*. Energy Conversion and Management, 2004. **45**(5): p. 651-671.
6. Katikaneni, S.P.R., J.D. Adjaye, and N.N. Bakhshi, *Performance of Aluminophosphate Molecular Sieve Catalysts for the Production of Hydrocarbons from Wood-Derived and Vegetable Oils*. Energy & Fuels, 1995. **9**(6): p. 1065-1078.
7. Piskorz, J., D.S. Scott, and D. Radlein, *Composition of Oils Obtained by Fast Pyrolysis of Different Woods*, in *Pyrolysis Oils from Biomass*. 1988, American Chemical Society. p. 167-178.
8. Sharma, R.K. and N.N. Bakhshi, *Upgrading of pyrolytic lignin fraction of fast pyrolysis oil to hydrocarbon fuels over HZSM-5 in a dual reactor system*. Fuel Processing Technology, 1993. **35**(3): p. 201-218.
9. Sharma, R.K. and N.N. Bakhshi, *Upgrading of wood-derived bio-oil over HZSM-5*. Bioresource Technology, 1991. **35**(1): p. 57-66.
10. Mathews, J.F., et al., *Upgrading of aspen poplar wood oil over HZSM-5 zeolite catalyst*. The Canadian Journal of Chemical Engineering, 1985. **63**(4): p. 686-689.
11. Nguyen, T.S., et al., *Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts*. Biomass and Bioenergy, 2013. **48**(0): p. 100-110.
12. Suzuki, T., H. Ohme, and Y. Watanabe, *Alkali metal catalyzed carbon dioxide gasification of carbon*. Energy & Fuels, 1992. **6**(4): p. 343-351.
13. Di Blasi, C., C. Branca, and A. Galgano, *Effects of Diammonium Phosphate on the Yields and Composition of Products from Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2006. **46**(2): p. 430-438.
14. Di Blasi, C., C. Branca, and A. Galgano, *Thermal and catalytic decomposition of wood impregnated with sulfur- and phosphorus-containing ammonium salts*. Polymer Degradation and Stability, 2008. **93**(2): p. 335-346.
15. Di Blasi, C., A. Galgano, and C. Branca, *Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2009. **48**(7): p. 3359-3369.
16. Wang, J., et al., *Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass*. Thermochemica Acta, 2006. **444**(1): p. 110-114.
17. Samolada, M.C., A. Papafotica, and I.A. Vasalos, *Catalyst Evaluation for Catalytic Biomass Pyrolysis*. Energy & Fuels, 2000. **14**(6): p. 1161-1167.
18. Nguyen, T.S., et al., *Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts*. Bioresource Technology, 2013. **142**(0): p. 353-360.
19. Graboski, M.S. and R.L. McCormick, *Combustion of fat and vegetable oil derived fuels in diesel engines*. Progress in Energy and Combustion Science, 1998. **24**(2): p. 125-164.

20. Huber, G.W. and A. Corma, *Synergies between Bio- and Oil Refineries for the Production of Fuels from Biomass*. Angewandte Chemie International Edition, 2007. **46**(38): p. 7184-7201.
21. Brem, G. and E.A. Bramer. *PyRos: a new flash pyrolysis technology for the production of bio-oil from biomass residues*. in *International Conference & Exhibition Bioenergy Outlook*. 2007. Singapore.
22. Li, C.L., et al., *Coke formation on an industrial reforming Pt–Sn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst*. Catalysis Letters, 2000. **65**(4): p. 209-216.
23. Maher, K.D. and D.C. Bressler, *Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals*. Bioresource Technology, 2007. **98**(12): p. 2351-2368.
24. Lappas, A.A., et al., *Biomass pyrolysis in a circulating fluid bed reactor for the production of fuels and chemicals*. Fuel, 2002. **81**(16): p. 2087-2095.
25. Demirbas, A., *Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues*. Journal of Analytical and Applied Pyrolysis, 2004. **72**(2): p. 243-248.
26. Diebold, J.P., *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils*. , N.R.E. Laboratory, Editor. 2000.
27. Huber, G.W., et al., *Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates*. Science, 2005. **308**(5727): p. 1446-1450.
28. Climent, M.J., et al., *Mesoporous Materials as Catalysts for the Production of Chemicals: Synthesis of Alkyl Glucosides on MCM-41*. Journal of Catalysis, 1999. **183**(1): p. 76-82.
29. Huber, G.W., S. Iborra, and A. Corma, *Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering*. Chemical Reviews, 2006. **106**(9): p. 4044-4098.
30. Xu, J., et al., *Rice husk bio-oil upgrading by means of phase separation and the production of esters from the water phase, and novolac resins from the insoluble phase*. Biomass and Bioenergy, 2010. **34**(7): p. 1059-1063.
31. Guo, Y., et al., *Review of catalytic supercritical water gasification for hydrogen production from biomass*. Renewable and Sustainable Energy Reviews, 2010. **14**(1): p. 334-343.
32. Demirbas, A., *Hydrogen Production from Biomass via Supercritical Water Gasification*. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 2010. **32**(14): p. 1342-1354.
33. Achten, W.M.J., et al., *Jatropha bio-diesel production and use*. Biomass and Bioenergy, 2008. **32**(12): p. 1063-1084.
34. Sujatha, M., T.P. Reddy, and M.J. Mahasi, *Role of biotechnological interventions in the improvement of castor (*Ricinus communis* L.) and *Jatropha curcas* L.* Biotechnology Advances, 2008. **26**(5): p. 424-435.
35. Knothe, G., O. Dunn Robert, and O. Bagby Marvin, *Biodiesel: The Use of Vegetable Oils and Their Derivatives as Alternative Diesel Fuels*, in *Fuels and Chemicals from Biomass*. 1997, American Chemical Society. p. 172-208.
36. Pütün, A.E., A. Özcan, and E. Pütün, *Pyrolysis of hazelnut shells in a fixed-bed tubular reactor: yields and structural analysis of bio-oil*. Journal of Analytical and Applied Pyrolysis, 1999. **52**(1): p. 33-49.

37. Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils State of the Art for the End Users*. Energy & Fuels, 1999. **13**(4): p. 914-921.





## CHAPTER 6:

# Effect of $\text{Na}_2\text{CO}_3$ on primary decomposition kinetics of wood pyrolysis in novel vortex thermogravimetric analyser

**Abstract:** Effect of  $\text{Na}_2\text{CO}_3$  catalysts system on primary reaction kinetics of biomass pyrolysis has been investigated in a novel thermogravimetric vortex reactor. About 40 wt. %  $\text{Na}_2\text{CO}_3$  was impregnated onto the wood using wet and dry impregnation methods. The effect of the catalyst, the temperature and impregnation methods have been studied. The temperature and catalyst have significantly altered the primary reaction kinetics of the wood and decreased the activation energy resulting in a faster thermal degradation of wood. The catalytic effect to increase the primary reaction rates was enhanced with an increasing pyrolysis temperature. The wet impregnation of  $\text{Na}_2\text{CO}_3$  was more effective to alter the primary reaction kinetics of biomass pyrolysis compared to the dry impregnation.

## 6.1 Introduction

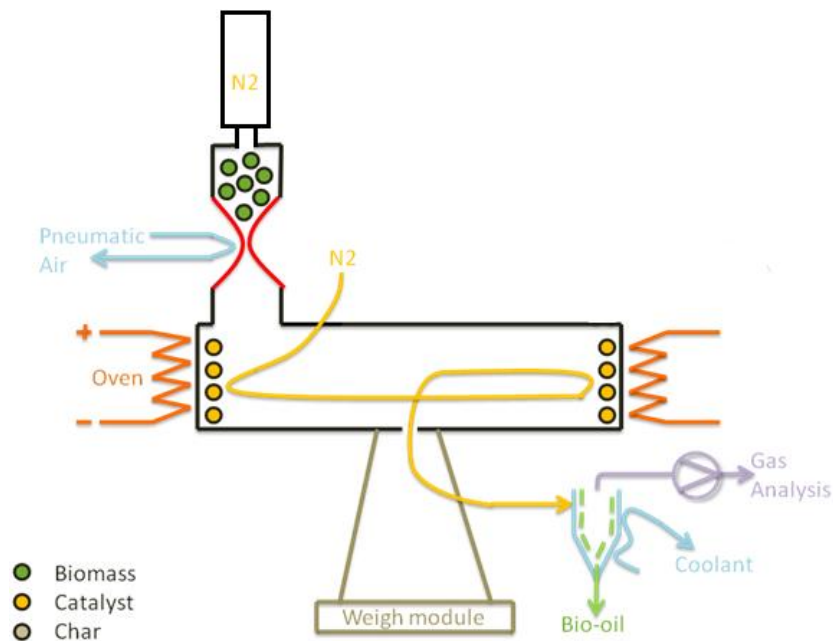
Flash pyrolysis is a simple process to convert biomass into a liquid, gas and solid product, and there is a considerable progress in catalyst development to improve the quality of pyrolysis-oil (hereinafter "bio-oil"). Recently alkali metal based catalyst systems gained interest for catalytic pyrolysis of biomass to produce high value bio-oil [1-3]. A majority of these studies is focused on the effect of alkali compounds on the biomass pyrolysis products but less attention for the effect of these alkali catalysts on the primary reaction kinetics of biomass conversion. It is believed that wet impregnated alkali metal can influence the primary decomposition reaction and can control the nature of biomass thermal degradation products. Di Blasi et al. found that wet impregnated alkali compounds including  $\text{Na}_2\text{CO}_3$  lowered the temperatures of biomass devolatilization and reduced the biomass conversion time [4-7]. Wang et al. found the similar effect that wet impregnated  $\text{Na}_2\text{CO}_3$  made de-volatilization of biomass occur at lower reaction temperatures [8]. In practical applications, wet impregnation of alkali metals pose technical and economic challenges and physical mixing of alkali metals is an easy and economical way for their implementation in catalytic pyrolysis of biomass. Wang et al. have studied the effect of dry impregnated  $\text{Na}_2\text{CO}_3$  on slow pyrolysis of pine wood and found the decomposition of hemicellulose and cellulose occurred at lower temperature, which indicates that dry impregnation also has impact on primary decomposition reaction of biomass [9]. These preliminary investigations indicate that  $\text{Na}_2\text{CO}_3$  has an effect on the primary reaction of biomass conversion but still lacking data for the reaction kinetics for the biomass flash pyrolysis in case of wet and dry impregnation of  $\text{Na}_2\text{CO}_3$  and the effect of operating variables e.g. temperature on the biomass flash pyrolysis. Recent work by authors [1-3], shows that  $\text{Na}_2\text{CO}_3$  is a promising catalyst for the production of bio-oil with a good fuel quality by flash catalytic pyrolysis of biomass and made it essential to further investigate the effect of  $\text{Na}_2\text{CO}_3$  on the primary reaction kinetics of biomass pyrolysis.

Typically, standard thermogravimetric analyzers (TGA) are used to determine the reaction kinetics but in these TGA's biomass particles sense a low heat transfer rate and thus pose problems to use standard TGA to determine the reaction kinetics of biomass flash pyrolysis in an accurate way. To overcome this design challenge, Bramer et al. have demonstrated a novel thermogravimetric vortex reactor to determine the primary pyrolysis rate of biomass thermal degradation where the novel reactor design achieved high heating rates required for biomass flash pyrolysis and the biomass conversion measured directly over time [10]. In the current work, this novel cyclonic TGA has been used to determine the effect of  $\text{Na}_2\text{CO}_3$  on primary reaction kinetics of wood pyrolysis. The effect of temperature and the measured kinetics of the primary thermo-chemical degradation of  $\text{Na}_2\text{CO}_3$  impregnated wood have been compared with those of untreated wood. Furthermore, the effect of different methods of  $\text{Na}_2\text{CO}_3$  impregnation (wet and dry) onto the wood has been investigated.

## 6.2 Methodology

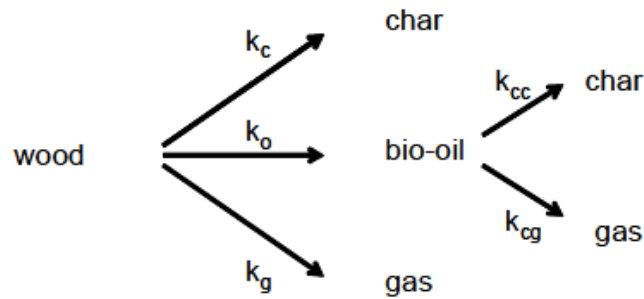
Experiment setup is presented in **Figure 26**. The cyclonic reactor has a cylindrical shape and the inert gas (nitrogen) is supplied in tangential direction at a given flow rate. The reactor is covered with an electric oven to provide the heat of pyrolysis. The gaseous pyrolysis products leave the cyclonic reactor at its bottom center. A batch of wood particles

(typically 1 gram) is injected to the side wall of the reactor with a pulse of nitrogen. The wood particles that enter the reactor are forced to the periphery of the reactor and swirl along the reactor wall because of the drag force of the swirling gases on the particles. This creates an infinite long solid residence time, on the other hand pyrolysis products, vapors and gases, immediately leave the reactor via the central bottom exit. A high degree of mixing is obtained as the particles swirl along the reactor wall. Wood particles are forced to be in close contact with the heated wall and the surrounding gases, which ensures the high heat rates obtained in this novel reactor. The whole reactor system is placed on a very sensitive balance, isolated from the surrounding environment, and the biomass conversion rate is determined by continuously measuring the biomass weight loss over time during the pyrolysis process.



**Figure 26:** Schematic of the TGA reactor setup

The reaction model, experimental setup and methodology to determine the primary kinetics for the pyrolysis of the wood have been described in detail by [10]. It is the same methodology as described by Di Blasi et al. [11] to obtain the kinetics for the pyrolysis of the wood and has been used in several studies. In reality, the cracking of biomass is a very complex process with different reaction paths for the three products (bio-oil, gas and char). Also, a higher temperatures and a longer residence time of the bio-oil vapors may result in secondary cracking of the vapors into char and gas, as seen in **Figure 27** [12].



**Figure 27:** Biomass cracking

If there is no limitation of mass and heat transfer, it can be assumed that the reaction rate is kinetically controlled [10]. This means that the reaction time is only determined by its primary kinetics and not by other influences. Then the cracking of a biomass particle can be represented by a single order reaction, shown by equation (1).

$$\dot{m} = k * (m - m_c) \quad (1)$$

With:

$m$  = mass of biomass [kg]

$m_c$  = mass of remaining char [kg]

$k$  = overall first order reaction rate constant for the decomposition of biomass [ $s^{-1}$ ]

$\dot{m} = dm/dt$

The overall first order reaction rate constant can be described by the Arrhenius equation (2):

$$k = A_0 e^{\frac{-E_a}{R*T}} \quad (2)$$

With:

$A_0$  = pre-exponential constant [ $s^{-1}$ ]

$E_a$  = activation energy [J/mole]

$R$  = gas constant [J/(mole\*K)]

$T$  = reaction temperature [K]

By measuring the change of mass over time, the conversion of biomass can be calculated by equation (3).

$$\zeta = \frac{m_o - m}{m_o - m_c} \quad (3)$$

$\zeta$  =Biomass conversion

Putting equation (1) and (3) together gives:

$$\zeta = 1 - e^{-k*t} \quad (4)$$

From this the overall first order reaction rate constant  $k$  can be experimentally found.

### 6.2.1 Biomass:

The biomass used for the experiments consisted of wood fibres commercially available with trade name LIGNOCEL by J. RETTENMAIER & SÖHNE GmbH. The biomass particle size varied from 0.1 to 1 mm. As biomass particle size can limit the heating rates of biomass, biomass was sieved and the particle size range from 125 to 250  $\mu m$  was used for the cyclonic TGA experiments. The particle size range from 125 to 250  $\mu m$  was selected based on preliminary experiments to achieve a high enough heating rates by using small

particle sizes [10]. The ultimate (wet basis) and proximate analyses of Lignocel are presented in **Table 34**.

**Table 34:** Ultimate and proximate analysis of the biomass feedstock<sup>24</sup>

	C [%]	H [%]	N [%]	O <sup>25</sup> [%]	Moisture [%]	Volatiles [%]	Fixed C. [%]	Ash [%]	LHV [MJ/kg]
Lignocel	49.2	5.7	0.1	45.0	6.5	76.4	13.6	3.5	16.6

### 6.2.2 Catalyst impregnation methods:

Na<sub>2</sub>CO<sub>3</sub> (ACS reagent grade >99.5%) was obtained from Sigma Aldrich and impregnated onto wood via wet and dry impregnation methods. For wet impregnation, a saturated solution of sodium carbonate was prepared at room temperature (21 g Na<sub>2</sub>CO<sub>3</sub> per liter of water) and heated to 60 °C. Na<sub>2</sub>CO<sub>3</sub>. Biomass was added to the Na<sub>2</sub>CO<sub>3</sub> solution and vigorously stirred for 15 minutes at room temperature. The catalyst treated biomass sample was put in an oven for 24 hours at 75 °C to evaporate the water. For dry impregnation, the catalyst was mixed with biomass and ball milled for 24 hours. For both impregnation methods, a 40 wt-% of Na<sub>2</sub>CO<sub>3</sub> was used with balance of biomass. About 1 g of biomass sample was used for the thermal pyrolysis experiments and 1.4 g of sample (biomass impregnated with 40 wt-% Na<sub>2</sub>CO<sub>3</sub>) was used for the catalytic pyrolysis experiments.

### 6.3 Results and discussion:

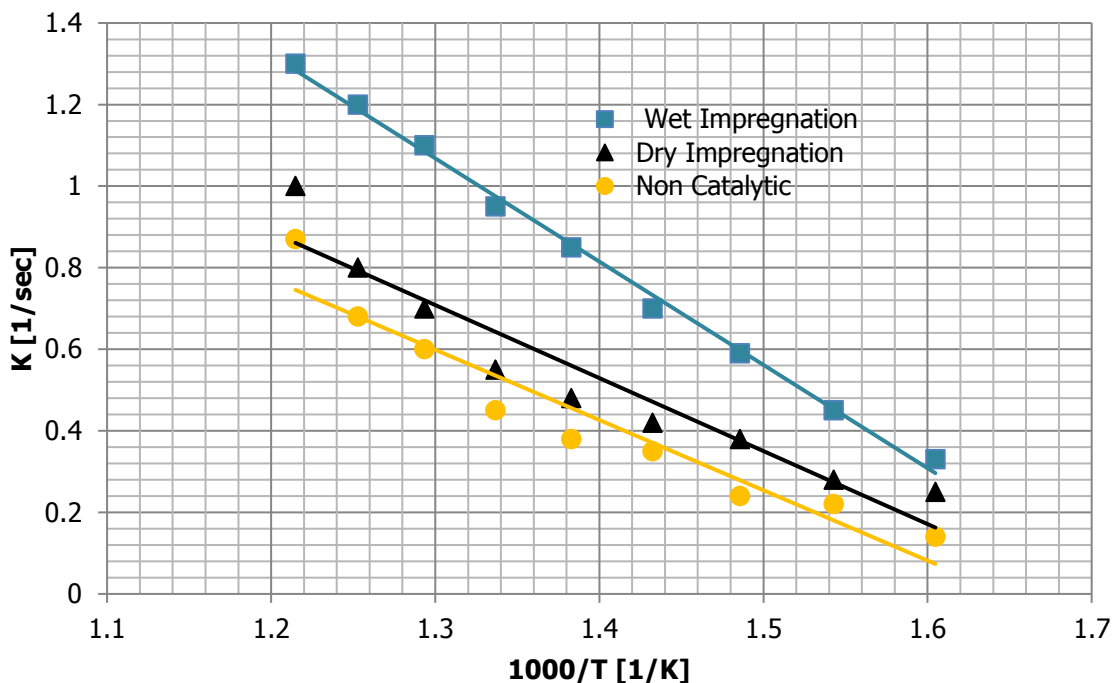
Non-Catalytic and catalytic experiments were conducted at 350, 400, 425, 450, 475, 500, 525 and 550 °C. For a constant heating rate, we can plot the pseudo first-order kinetic constant vs temperature with the relationship between time and temperature. The results are plotted in **Figure 28**, which shows the influence of the reaction temperature, the catalyst and catalyst impregnation method on the kinetic constant.

It can be seen that all these parameters have a very clear impact on the primary biomass degradation reaction kinetics. The primary reaction rates are higher at higher temperature, and catalyst impregnation enhances the reaction rate. As expected, wet impregnated catalysts have a higher effect on the primary reaction rates compared to the dry impregnation. Dry impregnated catalysts do not penetrate as deep into the biomass particle as in case of wet impregnated catalysts. Secondly, the dry impregnated catalysts can be detached from the biomass particle surface as soon as they come across the high gas swirl in the TGA reactor. Because of these reasons, dry impregnated Na<sub>2</sub>CO<sub>3</sub> is less likely to influence primary decomposition reaction of biomass pyrolysis, and their catalytic activity is likely to be limited to secondary reforming of bio-oil vapors but that cannot be studied with the current configuration of the TGA reactor. Wet impregnated Na<sub>2</sub>CO<sub>3</sub> is

<sup>24</sup> all values are in weight % except LHV i.e. MJ/kg

<sup>25</sup> by difference

likely to have main influence on the primary decomposition reaction of biomass pyrolysis as the sodium ion is relatively small, and it can penetrate into the biomass textures using the wet impregnation, and it can break the intermolecular hydrogen bridges while soaking or pyrolysis/temperature. As well, sodium is basic in nature and it can cause extraction of some low molecular compounds in the wood. Sodium can also react with cellulose, hemicellulose, and lignin that are major components of lignocellulosic materials e.g. wood. It is evident from **Figure 28** that wet impregnated  $\text{Na}_2\text{CO}_3$  has significantly increased the primary decomposition/reaction rates and made devolatilization occur faster. The catalytic effect of  $\text{Na}_2\text{CO}_3$  is enhanced by increasing the pyrolysis temperature. Dry impregnated  $\text{Na}_2\text{CO}_3$  has also enhanced the primary reaction kinetics of wood pyrolysis, but its catalytic effect is less pronounced compared to the wet impregnated  $\text{Na}_2\text{CO}_3$ .



**Figure 28:** Arrhenius plot for the first order decomposition reaction kinetics measured in the cyclonic TGA

## 6.4 Conclusions:

The effect of  $\text{Na}_2\text{CO}_3$  catalyst system on the primary reaction kinetics of biomass pyrolysis has been investigated in a novel thermogravimetric vortex reactor. 40 wt. %  $\text{Na}_2\text{CO}_3$  was impregnated onto the wood using wet and dry impregnation methods. The effect of the catalyst, the temperature and impregnation methods have been presented. The catalyst has significantly increased the primary reaction kinetics of the wood and decreased the activation energy resulting in a faster thermal degradation of wood during pyrolysis. The catalytic effect on the primary reaction rates was enhanced with increasing pyrolysis temperature. The wet impregnation of  $\text{Na}_2\text{CO}_3$  was much more effective to alter the primary reaction kinetics of biomass pyrolysis compared to the dry impregnation.

## 6.5 References

1. Imran, A., et al., *Catalytic flash pyrolysis of oil-impregnated-wood and jatropa cake using sodium based catalysts*. Journal of Analytical and Applied Pyrolysis.
2. Imran, A., et al., *High quality bio-oil from catalytic flash pyrolysis of lignocellulosic biomass over alumina-supported sodium carbonate*. Fuel Processing Technology, 2014. **127**(0): p. 72-79.
3. Nguyen, T.S., et al., *Conversion of lignocellulosic biomass to green fuel oil over sodium based catalysts*. Bioresource Technology, 2013. **142**(0): p. 353-360.
4. Di Blasi, C., A. Galgano, and C. Branca, *Influences of the Chemical State of Alkaline Compounds and the Nature of Alkali Metal on Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2009. **48**(7): p. 3359-3369.
5. Di Blasi, C., C. Branca, and A. Galgano, *Thermal and catalytic decomposition of wood impregnated with sulfur- and phosphorus-containing ammonium salts*. Polymer Degradation and Stability, 2008. **93**(2): p. 335-346.
6. Di Blasi, C., C. Branca, and A. Galgano, *Effects of Diammonium Phosphate on the Yields and Composition of Products from Wood Pyrolysis*. Industrial & Engineering Chemistry Research, 2006. **46**(2): p. 430-438.
7. Di Blasi, C., A. Galgano, and C. Branca, *Effects of Potassium Hydroxide Impregnation on Wood Pyrolysis*. Energy & Fuels, 2009. **23**(2): p. 1045-1054.
8. Wang, J., et al., *Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass*. Thermochimica Acta, 2006. **444**(1): p. 110-114.
9. Wang, Z., et al., *Pyrolysis of pine wood in a slowly heating fixed-bed reactor: Potassium carbonate versus calcium hydroxide as a catalyst*. Fuel Processing Technology, 2010. **91**(8): p. 942-950.
10. Bramer, E.A., M.R. Holthuis, and G. Brem. *A novel thermogravimetric vortex reactor for the determination of the primary pyrolysis rate of biomass Conversion*. in *Proceedings Conference on Science in Thermal and Chemical Biomass*. 2004. Vancouver, Canada.
11. Di Blasi, C., *Modeling intra- and extra-particle processes of wood fast pyrolysis*. AIChE Journal, 2002. **48**(10): p. 2386-2397.
12. Shu, X., et al., *Determination of less combustible constituents and investigation of their combustion characteristics in coals*. Fuel Processing Technology, 2000. **68**(3): p. 223-235.





## CHAPTER 7:

# General conclusions and future Outlook

### 7.1 Conclusions and discussion

In chapter 2, a literature review showed that zeolites reduce the concentration of oxygenated compounds present in biomass pyrolysis bio-oil via de-oxygenation reactions like dehydration, de-carbonylation and decarboxylation, with an increase in hydrocarbon and/or aromatic species. Another credit to zeolites is a decreased molecular weight of the bio-oil because of cracking of lignin derived compounds. However, the drawbacks of applying the relatively small pore zeolites are a significant decrease in yield of organic phase of the bio-oil due to an increase in the production of water and gases, and a rapid catalyst deactivation by coke deposition. Compared to zeolites, the larger pore size of aluminosilicates reduced the catalyst deactivation and achieved a relatively higher organic yield. However, in some cases the aluminosilicates performed no better than the conventional zeolites. In general, these mesoporous catalysts showed less activity compared to ZSM-5 under the same conditions, however, a careful tuning of the pore size and acidity could improve product selectivity. Studies on the effects of added alkaline compounds on the pyrolysis of lignocellulosic material are not extensive and their catalytic effects on biomass pyrolysis products characteristics are not systematically investigated. A detailed analysis of the bio-oil characteristics is lacking, which is needed to evaluate the potential of alkaline compounds as a catalyst for biofuels production. Nevertheless, some qualitative features are well evident that alkali metals cause an increase in the yield of char, gas and water and a reduction in the organic liquid with an enhancement in the activity of dehydration, decarboxylation, and charring reactions. Alkali metals caused a reduction in higher molecular weight compounds such as levoglucosan towards lower molecular weight compounds, associated with the increased yields of gas. Condensed fragments in the char structure suggest that not only primary reactions but secondary reactions are also affected. The preliminary results show the potential of alkaline earth metals for de-oxygenation of bio-oil, for production of hydrocarbons, and for reduction of undesired compounds with acids at the top, but further systemic studies are required to explore their full catalytic activity for the production of biofuels.

In Chapter 3, an experimental study showed that modified zeolites can perform de-oxygenation, however, at the cost of a reduced organic liquid yield because of secondary cracking reactions of vapors leading to the formation of gases and water. Nevertheless, in an integrated process the gas and char generated during the catalytic pyrolysis can

provide the heat required for the pyrolysis step or it can be used for biomass drying. In general, increasing the acidity of zeolites favored the formation of the desired compounds such as phenols and furans and reduced the most deleterious components in the bio-oil such as acids. However some of the undesired components in the bio-oil such as ketones, aldehydes increased with an increasing acidity of zeolites. The overall performance of modified zeolites is not up to the mark to tailor the desired bio-oil properties and they cannot be the first choice catalyst for in-situ upgrading of bio-oil. Online fractionation via staged condensation proved to be a successful technique to produce high calorific value bio-oil with very low water content of 10 wt.%. It can be concluded that fractionation is a promising cheap downstream approach to tailor the bio-oil properties. The integrated process of catalytic pyrolysis and in-situ fractionation can be used for the production of tailor made biofuels and/or bio-chemicals.

The novel catalyst  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  is experimentally studied in chapter 4, and proved to be a promising catalyst to improve the deleterious properties of bio-oil from pyrolysis. A high level of de-oxygenation is achieved using both experimental modes of operation, post treatment of pyrolysis vapor and in-situ upgrading of pyrolysis vapors. The catalytically produced bio-oil has a high calorific value and is rich in valuable chemical compounds. Acids in the bio-oil are completely removed resulting in a neutral pH bio-oil that can improve handling and stability characteristics of the bio-oil. Such a remarkable improvement in quality of bio-oil is of high significance towards production of a green fuel precursor. This high energy bio-oil, rich in organics, with low water and oxygen content can be upgraded via hydrotreatment for fuel application.

Sodium based catalyst systems have been investigated in chapter 5 aiming to produce a hydrocarbon rich bio-oil. Catalytically bio-oil produced by pyrolysis of vegetable oil-impregnated-wood and jatropha cake using  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalysts has a very low oxygen content, a water content as low as 1 wt.%, a neutral pH, and a high calorific value that is very close to that of transportation fuels. This bio-oil consists of high value chemical compounds for fuel application such as hydrocarbons. The incorporation of triglycerides in wood enhances the formation of hydrocarbons. Due to technical challenges associated with the use of pure  $\text{Na}_2\text{CO}_3$  such as downstream process recovery of catalysts and due to a comparative poor performance of  $\text{Na}_2\text{CO}_3$ , the  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalytic system could be a first choice for commercial production of bio-oil.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  also showed a good catalytic activity after regeneration. Neutral pH and absence of aldehydes will improve both handling and stability characteristics of the bio-oil.

Characteristics of bio-oil obtained from non-catalytic pyrolysis of wood (Thermal), and from catalytic ( $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ) pyrolysis of wood and oil-impregnated wood are summarized in **Table 35**. It is evident from the characteristics of the catalytic bio-oil that  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  is an efficient de-oxygenation catalyst and can selectively remove the oxygen from the bio-oil. A high quality bio-oil can be produced using  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  in a single step of catalysis-pyrolysis eliminating the need for condensation and re-evaporation of bio-oil in a post-treatment step. The incorporation of triglycerides in wood leads to an added improvement in the chemical composition of bio-oil and enriches its hydrocarbon content, increases its heating value, and increases the water immiscibility that leads to a spontaneous separation of the organic phase of the pyrolytic liquid leading to a 1% water

content. This hydrocarbons rich, almost water free, neutral pH bio-oil can be an attractive precursor for refining to produce alternative fuels.

**Table 35:** Characteristics of bio-oil obtained from non-catalytic pyrolysis of wood (Thermal) and catalytic pyrolysis of wood and oil-impregnated wood.

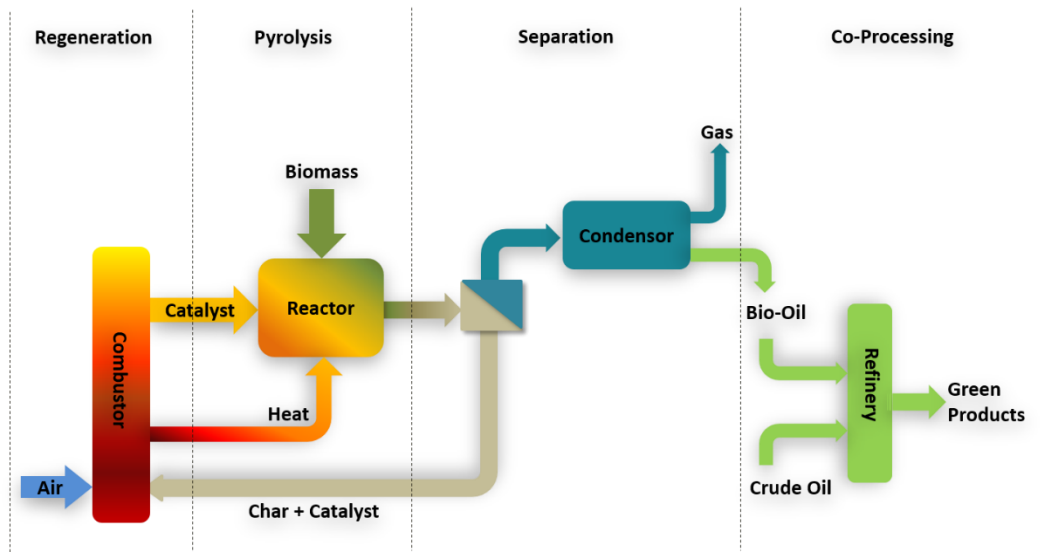
Characteristics	Thermal pyrolysis	Catalytic pyrolysis of wood	Catalytic pyrolysis of oil-impregnated-wood
Water content (wt.%)	31.5	5.8	1.0
C (wt.%, dry)	47.8	75.5	79.4
H (wt.%, dry)	6.2	7.6	9.8
O (wt.%, dry)	45.4	16.4	9.9
HHV (MJ kg <sup>-1</sup> )	17.8	36.1	38.8
Acidity as mg of KOH/gm	159	3.45	4.16
pH	2.2-2.4	6.3	6.5

## 7.2 Outlook and Recommendations:

The present study showed that a high value fuel precursor can be produced via catalytic pyrolysis of oil-impregnated-wood and jatropha cake using a  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  catalyst system. Oil-impregnated-wood is used only as a case study. In practice vegetable oil cannot be applied because of high prices in the edible oil market. Process economics could be further improved by using lower value oils such as waste cooking oil/fats or industrial oil. Although these waste oils are not widely available, they can be used as a minor supplement to the wood to produce a high quality bio-oil making the wood pyrolysis both economically and technically feasible.

As biofuels are more expensive than petroleum fuels, the economics for biomass pyrolysis are generally considered to be most favorable for biomass or plants which grow abundantly and require little cultivation in arid lands or industrial and agricultural wastes.

This work has presented that de-oiled seed cake from jatropha, a non-edible by-product, can be used as an alternative biomass resource for the production of high quality, hydrocarbon rich bio-oil in a single conversion process. This fuel precursor has a neutral pH, contains no or very less water, is rich in hydrocarbons, has a high calorific value and contains very few oxygenated compounds. Furthermore, the produced pyrolysis liquid shows spontaneous separation of water, an almost water free bio-oil can solve the miscibility problem with conventional fuels.



**Figure 29:** Schematic of biorefinery concept

Relatively low organic liquid yields obtained in the presence of  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  cannot be avoided if a high de-oxygenation of the bio-oil is required. This is caused by the loss of carbon and hydrogen associated with all routes of catalytic de-oxygenation. The catalyst properties and process parameters may be further optimized to increase the bio-oil yield. The amount of  $\text{Na}_2\text{CO}_3$  impregnated on  $\gamma\text{-Al}_2\text{O}_3$  also needs further optimization to maximize the de-carboxylation reaction and to suppress the de-hydration and de-carbonylation reactions.

The optimum type of catalytic pyrolysis reactor should have a long solid residence time for good conversion of the biomass and a short residence time for the vapors to avoid excessive secondary cracking and vapor contact with char and coke particle that can lead to unwanted gas and water formation. The novel cyclonic reactor system "PyRos" type can offer substantial advantage of a very short vapor residence time (less than half a second) over existing pyrolysis technologies e.g. fluidized bed reactor system, and can considerably improve the liquid yields and properties by avoiding excessive secondary cracking and contact of vapors with coke and char. The study conducted in Chapter 6, also showed that a cyclonic reactor system type has the advantage to increase the primary reaction kinetics of catalytic biomass pyrolysis. A PyRos" type reactor system can considerably optimize the solid conversion without significant secondary cracking to maximize the liquid yields. The preliminary investigations conducted around the globe show that catalysis can be implemented in existing pilot scale pyrolysis technologies that are able to be scaled up for commercial production of biofuels. A reactor concept with a mobile catalyst phase and integrated catalyst regeneration seems to be first line option for scale up of technology, as illustrated in **Figure 29** and the high quality bio-oil produced by integrated catalytic pyrolysis of biomass may be used as a co-feedstock for conventional refineries and existing infrastructure can be used for the production of sustainable transportation fuels.

There is no doubt that catalyst development is the key for a successful commercial production of biofuels and a breakthrough in catalyst development could lead to realization of biofuels production. The innovative catalyst system ( $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$ ) studied in this thesis can be applied at pilot scale reactor systems and has potential to tailor the bio-oil properties for fuels application and to overcome its deleterious properties.  $\text{Na}_2\text{CO}_3/\gamma\text{-Al}_2\text{O}_3$  shows promising regeneration characteristics and an FCC type pyrolysis operation, where combustion of coke deposited on the catalyst generates the energy required to run the endothermic cracking process, will solve the catalysts deactivation problems. Such an integrated heat recovery from combustible gases, char and coke can increase the overall process efficiency and economics.

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# CATALYST AND PROCESS DEVELOPMENT IS THE KEY FOR THE SUCCESS OF COMMERCIAL PRODUCTION OF BIOFUELS

Sodium based catalyst and the process developed has potential to tailor the desired bio-oil properties to produce a fuel precursor. A FCC type pyrolysis operation with an integrated heat recovery can increase the process efficiency & economics.

High quality bio-oil produced by integrated catalytic pyrolysis of biomass may be used as a co-feedstock for conventional refineries and existing infrastructure can be used for the production of sustainable transportation fuels.