Direct Liquefaction of Lignocellulose: Exploration, Design and Evaluation of Conceptual Processes

Supplementary material

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This supplementary book contains additional information for each chapter. The additional information is directly relevant to support the conclusions made in the thesis chapter, but was not included in the main thesis book for reasons of space and readability of the chapters.

The main thesis book can be downloaded here: <http://dx.doi.org/10.3990/1.9789036539500>

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Chapter 1

Introduction

1. Direct liquefaction processes

Apart from PERC, LBL and HTU processes, a few other processes namely CatLiq-process, STORS-process and TCP process, were also developed at various research laboratories.

The CatLiq-process was developed by a Danish company SCF Technologies, which uses both heterogeneous (ZrO_2) and homogeneous (K_2CO_3) catalysts as well as the properties of near-critical water (350°C and 25 MPa) to convert wet biomass into products. The products consist of an oil fraction (yield $\sim 30\text{--}35\%$), a fraction of water soluble components and a gas fraction¹. It also produces a solid phase which mainly consists of precipitated salts. This process is suitable for wet biomass containing more than 50 % water e.g. agricultural wastes, sewage sludge, manure etc. This process seems quite similar to the HTU process with some differences, for example HTU does not use any catalyst, but rely on post-upgrading of the produced bio-oil. In early 2011, the CatLiq technology was bought by Altaca Environmental Technologies & Energy company². The company is currently constructing a commercial plant and it is planned to put in operation by the end of 2015³⁻⁴.

In the late eighties, Water Engineering Research Laboratory, Ohio, USA, developed a prototype Sludge-To-Oil Reactor System (STORS), primarily as a waste-water treatment reactor system⁵. It largely processed undigested municipal sewage sludge (20 w% solids, 5 w% Na_2CO_3) and produced a heavy oil and char products suitable for use as a boiler fuel. A maximum oil yield of 36 w% was reported at $\sim 300^\circ\text{C}$ and ~ 15 MPa. Up to 73 % of the energy content of the feedstock was recovered as combustible products i.e. oil and char. Later, several other applications of so-called STORS processes were developed. In the early nineties, a demonstration plant with a capacity for processing up to 5 t/d as dewatered sludge was erected in Japan. In this plant dewatered sludge was liquefied and distilled under high temperature (300°C) and high pressure (10 MPa), and produced a heavy oil in an yield of 48 w% (combined yield of heavy oils in all product streams)⁶. Further development of this

technology was carried out by ThermoEnergy Corporation, and a demonstration plant was built in the city of Colton, California. The demonstration plant was completed in year 2000, and had demonstrated the Sludge-To-Oil Reactor System (STORS) in combination with Ammonia Recovery Process (ARP). The current status of the process is unknown⁷⁻⁸.

A company named, Changing world technologies (CWT) Inc. attempted to develop and commercialize the thermal depolymerization technology⁹, and referred to, by the company, as ‘Thermal Conversion Process (TCP)’¹⁰. In 1998, CWT started a subsidiary, Thermo-Depolymerization Process, LLC (TDP)¹⁰, which developed a demonstration and test plant (7 t/day) for the thermal depolymerization technology in Philadelphia. The process produced clean fuels, fertilizers and specialty chemicals from waste, by-products, or low-grade organic materials. An operating plant based on the CWT-TCP process was constructed in Carthage, MO, and processed around 200 t/d of turkey offal and grease continuously, and produced around 500 bbl/d of a renewable oil¹¹⁻¹². The process consisted three steps; 1) pulping into a water slurry and heating of the feedstock under pressure to a 1st stage reaction temperature (200-300°C), 2) flashing the slurry to a lower pressure and separating the 1st stage oil from water, and 3) heating the 1st stage oil to higher temperature (500°C) to crack the oil into light hydrocarbon leaving a solid product. It was reported that with full heat recovery, the overall energy efficiency can be above 85 % based on the heating value of the products and the dry feedstock. In 2009, the changing world technologies Inc. and its three subsidiaries filed for bankruptcy¹³.

A summary of the previous processes is provided in Table S 1.

Table S 1: Overview of direct thermal liquefaction processes in pilot or demonstration scale.

Process name	Developer/Supplier of the process	Raw material	T (°C)	P (MPa)	Catalyst /reactive gas	Plant scale	Oil yield (w%)	Heating value (MJ/kg)	Ref.
PERC-Process	Pittsburgh Energy Research Centre (USA)	Wood flour	330-370	21	Na ₂ CO ₃ , CO/H ₂	25 kg/h	53	34.5	¹⁴⁻¹⁵
LBL- Process	Lawrence Berkeley Laboratory (USA)	Wood flour	330–360	17–24	Na ₂ CO ₃ , CO/H ₂	1.8 kg/h	25-33	33.6	¹⁵⁻¹⁶
HTU-process	Shell Research Institute (NL)	Wet agricultural wastes, wood, straw	300–350	12–18	---	100 kg/h (wet) pilot plant	45	30-35	¹⁶⁻¹⁹
STORS process, USA	EPA's Water Engineering Research Laboratory, Cincinnati, Ohio, USA	Sewage sludge	275-300	85-150	N ₂ CO ₃	30 L/h	7-36	36	⁵
STORS process, Japan	Organo Corp.	Sewage sludge	300	10	Not known	5 t/day	48	31-39	⁶
CatLiq®-process	SCF Technologies A/S (DK)	DDGS	280–350	22–25	K ₂ CO ₃ , Zirconia	20 L/h pilot plant	30-35	N/A	¹
Thermal Conversion Process (TDP)	Changing World Technologies Inc. (USA)	Turkey offal and fats	200–300 (1 st stage) 500 (2 nd stage)	4.0	H ₂ SO ₄	200 t/day	Not known	N/A	¹¹

Chapter 2

Experimental and analysis

This chapter presents the materials, experimental set-ups, general experimental procedures and analytical equipment, definitions and calculation methods, used in this work.

**This chapter is a replication of chapter 2 of the main book. It is included here to make
this book standalone.**

1. Introduction

Here we describe frequently used materials, various experimental set-ups, general experimental procedures and different analytical equipment used in this work. Furthermore definitions of various terminologies and calculation methods used in this thesis are presented. Specific set-ups or modification of a set-up and specific procedures that were used for a specific part of the work are described in the corresponding chapter. In general, three different batch autoclave reactors having internal volumes of 9 mL, 45 mL and 560 mL were used. Pine wood was used as a biomass feedstock.

2. Materials and Methods

2.1. Materials

Pine wood was obtained from Rettenmaier Söhne GmbH (Germany). It was crushed to a particle size of < 0.5 mm and then was dried at 105°C for 24 h in an oven. The composition of the wood is listed in Table S 1. Guaiacol was obtained from Sigma Aldrich with a purity ≥ 98 %.

Table S 1: Pine wood composition²⁰.

Composition	Value	Composition	Value
chemical Analysis	w%, dry	ultimate analysis	w%, daf
Cellulose	35	C	46.6
hemicellulose	29	H	6.3
Lignin	28	O (by difference)	47.0
alkali metals	mg/kg, dry	N	0.04
K	34	S	0.06
Mg	134		
Ca	768		
total ash	2600		

2.2. Experimental set-ups

Three different batch autoclave reactors having internal volumes of 9 mL, 45 mL and 560 mL were used in this thesis. The 9 and 45 mL autoclaves were designed and build in-house with

very thin walls to allow very fast heating rate ($\sim 300^{\circ}\text{C}/\text{min}$ in the 9 mL autoclave) while the 560 mL autoclave was purchased from Autoclave Engineers. Safe operation was then achieved by operating them in an explosion-proof high-pressure room with external control of the unit. Details of these autoclaves are described below:-

9 and 45 ml autoclave set-up: The schematic diagram of the 9 mL set-up is shown in Figure S 1. The reactor was equipped with two orifices, one for a thermocouple and the other to connect a pressure indicator and a gate valve. Pressure and temperature of the reactor were recorded during the run. A pneumatic arm allowed to immerse and remove the autoclave into and from a hot fluidized sand bed. The sand bed was heated by an electric oven (with preheated fluidization gas). The set-up was equipped with a cylinder piston that could shake the 9 mL autoclave in a horizontal back-and-forth motion.

The 45 mL autoclave was equipped with a mechanical stirrer instead of a shaking unit. The rest of the set-up was same as the 9 mL autoclave set-up as shown in the Figure S 1.

Figure S 1: Schematic diagram of the experimental 9 mL batch autoclave reactor set-up.

560 mL Autoclave: The experimental set-up of the 560 mL autoclave reactor is shown in Figure S 2. It had a hollow-shaft mechanical stirrer and an electrical heating jacket. Pressure

and temperature of the reactor were monitored and recorded. The oven was controlled by a Eurotherm controller with an adjustable heating rate.

Figure S 2: Schematic diagram of the experimental 560 mL batch autoclave reactor set-up²¹.

2.3. Experimental procedure

Liquefaction: The experimental procedure for liquefaction experiments was as follow: a weighted amount of liquefaction solvent and, optionally, water were loaded and mixed after which a weighted amount of oven dried wood was added and mixed. The autoclave was tightly closed, flushed with nitrogen several times and pressurized to about 0.5 MPa of nitrogen. The shaking (9 mL) or stirring (45 and 560 mL) was turned on and the autoclave was immersed into the preheated fluidized sand bed (9 and 45 mL) or the electric heater was turned on (560 mL autoclave) which was set at 5-10°C above the target reaction temperature. The reaction time was started upon immersion of the autoclave in the sand bath. The reaction temperature was reached within ~1 min, ~5 min and ~60 min in the 9 mL, 45 mL and 560 mL autoclaves respectively. After the desired reaction time, the reactor was quenched in a cold water bath (9 and 45 mL) or cooled by natural convection (560 mL) which took < 2 min to drop below 100°C in the 9 and 45 mL autoclaves while it took ~30 min in the 560 mL autoclave. After the reactor was cooled, a gas sample was taken using a syringe. The autoclave was then opened after depressurizing. The remaining product (liquid and suspended solid) was filtered over filter with 6 µm pore size. The reactor was rinsed with acetone and the

resulting solution was passed over the 6 μm filter to wash the solid and collected in a dedicated flask. Acetone was then removed from the liquid product by vacuum evaporation and from the solid residue by atmospheric drying at 105°C. The overall procedure for products collection after liquefaction experiments in the autoclave is shown in Figure S 3.

Figure S 3. Overall procedure for products (solid, liquid and gas) collection after liquefaction experiments. In the bracket shows the analytical equipment used for analysis of the product.

The reaction temperature was defined as the end temperature and reaction time was defined as the time autoclave spent in the hot sand bath (9-45 mL) or the time when the electric heater was on (560 mL).

Refill runs: The experimental procedure for the refill runs was as follows: The feed charge was prepared by mixing the target amount of liquefaction solvent, wood, water (if required), and additive (if used). If additive was used it was added after dissolution in the desired amount of water. The feed solution was mixed thoroughly, loaded into an autoclave reactor. The reactor was closed tightly, flushed with nitrogen several times to remove any oxygen present in the system and pressurized to about 0.5 MPa of nitrogen. The stirrer was turned on and the autoclave was immersed into the preheated fluidized sand bed in case of 45 mL

autoclave while in case of 560 mL autoclave heater was turned on. The preheated sand-bed had a temperature of around 5-10°C higher than the desired reaction temperature. After the desired reaction time, the reactor was quenched in a cold water bath (45 mL) or cooled first by natural convection and then by sprinkling cold water on the reactor wall. The autoclave was subsequently cooled to ambient temperature and the gas sample was taken using a syringe. After depressurizing, the autoclave was then opened and a small sample of liquid was taken out (normally 1 g) for analysis. The remaining liquid was either used as a liquid solvent, as such or after filtration of solids, for the subsequent run. Subsequently a second weighted amount of dry pine wood mixed with a second weighted amount of water with/without additive was added to the autoclave and the autoclave was sealed and subjected to a second run. The refill procedure was repeated a few times, as specified later in the corresponding chapters. At the end of the last refill run, the remaining product (liquid and solids in suspension) was then collected in a glass vial and the reactor was rinsed with acetone to remove leftover liquid and solids deposits. The obtained acetone wash was filtered with filter paper of size 2-6 μm . The obtained product slurry (liquid + solid) was also filtered with a filter of pore size 2-6 μm , when necessary after dilution in some acetone to lower its viscosity. The obtained solid was dried at 105°C and atmospheric pressure. When an additive was used, the solid was further washed with water (to ensure removal of the additive) followed by acetone before drying at 105°C.

2.4. Analytical equipment and procedures

Gas phase:

Gas samples were analyzed with an off-line gas chromatography (Varian Micro GC CP-4900 with two analytical columns, 10 m Molsieve 5A and 10 m PPQ, using Helium as carrier gas).

Liquid phase:

In a typical liquefaction experiment, two phases were obtained, namely a large organic and a small aqueous phase. The organic phase was used for detailed analysis while the aqueous phase was only analyzed for its water concentration which typically was ~90 w%. Liquid samples (organic phase) were analyzed with Gel Permeable Chromatography (GPC; Agilent 1200 series, with RI and UV (wavelength: 254 nm) detectors), using 3GPC PLgel 3 μm MIXED-E columns connected in series. The column was operated at 40°C with tetrahydrofuran (THF) as solvent. Apparent molecular weights ($M_{w, \text{GPC}}$) were determined by

calibration with a solutions of polystyrene with molecular weight ranging from 162 to 30230 Da.

Low-molecular components present in a liquid were identified by using Gas Chromatography-Mass Spectrometry (GC-MS) with an Agilent GC-MS (GC 7890A MS 5975C).

Viscosity was measured using a rotational viscosity meter (Brookfield DV-E).

Elemental composition of a liquid was determined using Elemental analyzer (Interscience Flash 2000).

The chemical functionality of a liquid was investigated by means of Fourier Transform Infrared Spectrophotometer (FT-IR Bruker Tensor 27).

The water content of a liquid was determined by Karl Fisher titration (titrant: Hydranal composite 5, Metrohm 787 KFTitrino). The solvent used was a solution of methanol and dichloromethane mixed in a volumetric ratio of 3:1.

Higher heating value (HHV) was measured using a Bomb calorimeter (IKA C2000 basic).

pH and TAN were measured using an autotitrator (785 DMP Titrino, Metrohm).

Micro-carbon residue tests (MCRT) were performed following the ASTM D4530 standard.

The minerals were analyzed by using portable XRF (Niton CL3t GOLDD+) with measuring time of 30 s for main, low and light filters, and 5 s for high filter. For the analysis of minerals, the sample was first calcined at 600°C in air to obtain ash which was used for the analysis.

Solid phase:

The elemental composition of a solid was determined using Elemental analyzer (Interscience Flash 2000).

The chemical nature of a solid investigated by means of Fourier Transform Infrared Spectrophotometry (FT-IR Bruker Tensor 27).

Higher heating value (HHV) was measured using a Bomb calorimeter (IKA C2000 basic).

The minerals were analyzed by using portable XRF (Niton CL3t GOLDD+) using the same procedures as used for a liquid sample.

3. Definitions and calculations

Figure S 4 defines the steps and various streams of the liquefaction process studied in this thesis. Firstly wood is liquefied using a liquefaction solvent in a liquefaction reactor. The

reactor effluent is degassed and then filtered to remove the solid/char. Typically, two liquid phases are obtained namely a small aqueous phase and a large organic phase. The organic phase is referred to as ‘**Organic liquid effluent**’. The organic liquid effluent contains single-pass reactor product (from biomass) as well the liquefaction solvent. The heavy (bio-based) liquid product obtained after separation of the liquefaction solvent (e.g. by extraction or distillation, as explained later) is referred to as ‘**Bio-crude**’.

Figure S 4: Various processes and nomenclature of the streams involved during the liquefaction of wood.

Gas, liquid and solid yields are mostly reported as carbon-fraction of the wood intake (equation S.1-S.3) rather than the common weight fraction to avoid counting the oxygen content or water as valuable product for subsequent conversion to biofuel. Hence, the liquid yield on carbon basis can be considered as bio-crude yield from wood, upon neglecting the marginal loss of carbon in the small aqueous phase.

The gas yield is calculated using the gas composition, analyzed by the off-line GC, and the available gas volume at the end pressure and temperature (after cooling), using the ideal gas law. The available gas volume is defined as being the total volume of the reactor minus the volume of the liquid product.

The solid yield is determined based on the weight yield of the solid residue and its carbon content.

The liquid yield is obtained by difference.

$$Yield_{Solid} (\%) = \frac{M_{Acetone\ insoluble}}{M_{Wood\ intake\ (dry)}} \times 100 \quad (S.1)$$

$$Yield_{Gas} (\%) = \frac{M_{Gas\ formed}}{M_{Wood\ intake\ (dry)}} \times 100 \quad (S.2)$$

$$Yield_{Liquid} (\%) = 100 - Yield_{Solid} (\%) - Yield_{Gas} (\%) \quad (S.3)$$

Here M stands for total mass of the carbon present if yields are reported in C% but stands for the total mass if yields are reported in w%. It should be noted that, by doing so, all the

losses are attributed to the liquid and, hence, the liquid yield may be over-reported. However, the validity of the definition of the liquid yield (equation S.3) is checked and confirmed by recalculating the liquid yield of selected samples using their GPC analysis and a calibration line developed with a bio-crude sample that was freed from the guaiacol solvent by means of vacuum distillation (see next chapter). The yields calculation using equations 1-3 could suffer from inaccuracies due to reaction of the liquefaction solvent. However blank experiments are carried with only liquefaction solvents to show their contribution. In case of guaiacol as solvent, the contribution was found very marginal as no solid formation and a very small amount of gas formation ($< 0.5\text{ C\%}$ at 350°C) were observed.

The organic liquid effluent consists of the liquefaction solvent and the bio-crude. These two fractions are further defined based on their apparent molecular weight (as determined by GPC) as the solvent/guaiacol with $M_{W,\text{GPC}} < 180\text{ Da}$ and the bio-crude with $M_{W,\text{GPC}} > 180\text{ Da}$ as illustrated in Figure S 5. The bio-crude is further divided into two fractions namely ‘**Distillates**’ as $M_{W,\text{GPC}} < 1000\text{ Da}$ and ‘**Vacuum Residue**’ (VR) or ‘**Heavies**’ as $M_{W,\text{GPC}} > 1000\text{ Da}$, also illustrated in the Figure S 5. It should be noted here that in chapters 6 and 7, the definition of distillates also includes start-up liquefaction solvent.

Figure S 5: Definition of the various fractions of the organic liquid effluent based on GPC curve. Truncated peak at $\sim 100\text{ Da}$ represents the liquefaction solvent (guaiacol in this case, $M_w: 124\text{ Da}$).

The vacuum residue fraction is defined as the fraction of the bio-crude (solvent-free organic liquid effluent) that is found in the molecular weight range of the vacuum residue

($M_{W, GPC} > 1000$ Da) based on equation S.4. It assumes comparable response factor for the distillates and heavies.

$$\text{Vacuum residue fraction} = \frac{\text{Area corresponds to } M_{W, GPC} > 1000 \text{ Da}}{\text{Area corresponds to } M_{W, GPC} > 180 \text{ Da}} \quad (\text{S.4})$$

The molar mass cut-off of the bio-crude is set at 180 Da to exclude the solvent (Guaiacol, MW: 124 Da) and its eventual primary degradation products (e.g. 1, 2-dimethoxybenzene).

Conversion is defined by equation S.5 and selectivity of gas, liquid, VR and distillates are defined by equation S.6-S.9.

$$\text{Conversion (\%)} = 100 - \text{Yield}_{\text{Solid}} \quad (\text{S.5})$$

$$\text{Selectivity}_{\text{Gas}} = \frac{\text{Yield}_{\text{Gas}}}{\text{Conversion}} \quad (\text{S.6})$$

$$\text{Selectivity}_{\text{Liquid}} = \frac{\text{Yield}_{\text{Liquid}}}{\text{Conversion}} \quad (\text{S.7})$$

$$\text{Selectivity}_{\text{VR}} = \text{Selectivity}_{\text{Liquid}} \times \text{VR fraction} \quad (\text{S.8})$$

$$\text{Selectivity}_{\text{Distillates}} = \text{Selectivity}_{\text{Liquid}} - \text{Selectivity}_{\text{VR}} \quad (\text{S.9})$$

It should be mentioned that the apparent molecular weight of the distillates corresponds to that of refinery distillate + vacuum gasoil (or vacuum distillate) while that of vacuum residue corresponds to that of refinery vacuum residue²². Refinery terminology is used here to facilitate the translation into the refinery operation to be selected for upgrading of the bio-crude into a final biofuel.

The cumulative wood percentage is introduced as indicator for the approach to continuous solvent recycling in refill experiments. It represents the fraction of wood in the fresh intake, that is wood and fresh solvent (start-up + make-up). It is increasing towards 100 % upon successive refills. The cumulative wood percentage is calculated from the amount of fresh wood used in a given refill run, the cumulative amount of fresh wood processed by the recycle solvent and, when necessary, the amount of make-up solvent used in that specific run (equation S.10). Interestingly, the cumulative wood percentage also represents roughly the concentration of wood-derived components in the recycle solvent when the whole reaction effluent is recycled as reaction solvent.

$$\text{Cumulative wood in run 'i' (w\%)} = \frac{\text{Wood (g)} + \text{Recycle solvent (g)} \times \text{Cum. wood in run } i-1'(\text{w\%})/100}{\text{Wood (g)} + \text{Recycle solvent (g)} + \text{make-up solvent (g)}} \times 100 \quad (\text{S.10})$$

For the first run, recycle solvent is zero.

A graphical representation of the cumulative wood percentage with successive refill (recycle) runs is provided in Figure S 6, for a feed comprising of liquefaction solvent and wood in 55:30 ratio in all the refill (recycle) runs, with no addition of make-up solvent. The figure clearly shows that the cumulative wood percentage approaches towards 100 w% upon successive refill runs and reaches ~90 w% within 5 refill runs.

Figure S 6: Cumulative wood (w%) versus refill (recycle) run with a feed comprising of liquefaction solvent and wood in a 55:30 ratio with no addition of make-up solvent.

Chapter 3

Liquefaction of lignocellulose: Process parameters study to minimize heavy ends

1. GPC analysis

The liquid yields calculated using the GPC area and a calibration line constructed using a solvent-free organic liquid effluent, show a fairly good match with the liquid yields calculated by 100-gas-solid yield (C%) in the liquefaction experiments at different temperatures as shown in Figure S 1.

Figure S 1: Liquid yields calculated using GPC versus liquid yields calculated by 100-gas-solid yield (C%) in liquefaction experiments at different temperatures. Autoclave: 9 mL; τ : 20 min, Feed (w%); Guaiacol:Water:Wood = 60:20:20.

Figure S 2 and Figure S 3 show unnormalized GPC curves of the organic liquid effluents obtained with different heating rates and different water concentrations respectively. The molecular weight distributions of the organic liquid effluents, i.e. after normalization, do not seem to be affected by these two parameters.

Figure S 2: Apparent molecular weight distributions of the organic liquid effluents obtained after the liquefaction experiment in the 9 mL, 45 mL and 560 mL autoclave. T : 320°C, Feed (w%); for 9 mL and 45 mL, Guaiacol:Wood:Water = 60:20:20, for 560 mL, Guaiacol:Wood:Water = 70:20:10.

Figure S 3: Apparent molecular weight distributions of the organic liquid effluents obtained in the liquefaction experiment with different water concentrations. Autoclave: 9 mL; T : 320°C, Feed (w%); Guaiacol:Wood:Water = (80- X):20: X .

Figure S 4 shows the RI/UV ratio of the organic liquid effluents obtained after liquefaction of pine wood at different reaction times. A steep increase in the RI/UV ratio, after 10000 Da is due to a baseline artefact. The organic liquid effluents are richer in conjugated aromatic/unsaturated components than organosolv lignin, and may even show higher degree of conjugation. With increasing the reaction time, the degree of unsaturation and/or conjugation seems to further increase (seen in between 1000-8000 Da, Figure S 4).

Incomplete conversion of the wood leads to a higher RI/UV ratio compare to the complete conversion of the wood.

Figure S 4: RI/UV signal of the organic liquid effluents obtained after liquefaction of pine wood at different reaction times (a) Autoclave: 9 mL and (B) Autoclave: 45 mL. T : 320°C, Feed (w%); Guaiacol:Wood:Water = 60:20:20, Heating rate: 300°C/min (9 mL), 180°C/min (45 mL).

2. Product yields and Gas analysis

The product yields of the liquefaction experiments at different temperatures and at different reaction times in the 9 mL autoclave are provided in Table S 2.

Table S 2: Product yields of liquefaction experiments at different temperatures (T) and at different reaction times (τ) in the 9 mL autoclave. Feed (w%); Guaiacol:Wood:Water = 60:20:20.

T	τ	Liquid	Gas	Solid	Liquid	Gas	Solid
(°C)	(s)	(C%)			(w%)		
Effect of temperature							
250	1200	57.6	2.0	40.4	58.4	3.2	38.4
300	1200	93.3	5.8	0.8	90.5	8.9	0.6
320	1200	92.2	7.1	0.7	88.8	10.7	0.5
350	1200	90.5	8.3	1.1	87.2	12.0	0.8
370	1200	75.1	13.3	11.6	74.6	17.3	8.1
400	1200	--	--	71.6	--	--	43.3
320	1200	92.4	6.8	0.8	89.5	9.9	0.6
Effect of time							
320	100	55.9	2.6	41.5	58.4	1.3	40.3
320	200	80.2	4.9	14.9	77.0	7.4	15.5
320	300	94.7	4.8	0.6	92.5	7.1	0.4
320	400	94.4	4.5	1.0	92.6	6.7	0.7
320	500	93.9	5.4	0.7	91.6	7.9	0.5
320	900	94.2	5.8	0.1	91.3	8.6	0.1
320	1200	92.2	7.1	0.7	88.8	10.7	0.5
320	10800	91.9	7.6	0.5	88.4	11.3	0.3

As shown in Table S 3, the wood conversion is incomplete up to 200 s of reaction time. Once the wood conversion is complete, the product yields do not change much. The VR fraction is the highest for the reaction time of 200 s while there is no significant difference between the VR fractions obtained at reaction times of 400 s and 500 s.

Table S 3: Product yields of the liquefaction experiments with different reaction times (τ) in the 45 mL autoclave. T: 320°C, VR: Vacuum residue.

τ (s)	Yield (C%)			Mass balance (w%)	VR fraction
	Liquid	Solid	Gas		
200	26.5	71.3	2.2	92.7	0.48
400	85.6	9.0	5.4	100.9	0.33
500	87.6	7.4	5.1	97.5	0.32

Figure S 5 shows the gas yields obtained during the liquefaction runs at different temperatures. In the gas phase, CO₂, CO, H₂ and CH₄ are the major compounds found. The produced gas phase consists of CO₂ and CO up to temperature 350°C, and above 350°C, CH₄ also becomes significant. The yields of these gases increase with temperature. However, the yield of H₂ is hardly affected by temperature and remains very low. A significant part of CH₄ may be coming from the solvent through solvent decomposition which was observed to be more severe with temperature. The gas yield in the blank experiment was very low (0.32 w% of guaiacol) and the gas composition was dominated by methane (89 vol%) with a small amount of CO (5 vol%), CO₂ (5 vol%) and H₂ (1 vol%). No solid formation was observed in the blank experiment.

$$\text{Yield (H\%)} = \frac{\text{Mass of hydrogen in the gas}}{\text{Mass of hydrogen in the wood}} \times 100 \quad (\text{S.1})$$

Figure S 5: Yields of different gases produced during liquefaction of pine wood at different temperatures. τ : 20 min. Hydrogen yield is calculated based on hydrogen present in the feed wood. Autoclave: 9 mL; Feed (w%); Guaiacol:Wood:Water = 60:20:20.

Figure S 6 shows the gas yields during liquefaction at different reaction times. CO_2 , CO and H_2 are dominant in the gas phase. Methane was also produced in a very small amount till 900 s, and becomes significant at a longer reaction time of 3 h. The yield of CO follows a slight incremental path. It is likely that an increase in CO_2 at later stage of reaction is due to the decarboxylation of organic acids (formed during the liquefaction).

Figure S 6: Yields of different gases produced during liquefaction of pine wood at different reaction times; T : 320°C . Hydrogen yield is calculated based on hydrogen present in the feed wood. Autoclave: 9 mL; Feed (w%); Guaiacol:Wood:Water = 60:20:20.

3. Temperature and pressure profiles

Figure S 7 shows the temperature and pressure profiles obtained during a liquefaction experiment in the 9 mL autoclave. Initially, the temperature increases to around 320°C and then it suddenly decreases and again it increases till it reaches the set-point temperature. It is likely that the temporary dip in the temperature is due to two reasons: (i) evaporative cooling i.e. rapid boiling of water (boiling point of water is $\sim 255^\circ\text{C}$ at 40 bar pressure) and/or (ii) some endothermic reactions e.g. dehydration reaction that makes unsaturated compounds and releases water. The major change in the reactor pressure is mainly happening till around 260 s. Similar temperature and pressure profiles were also observed in the other experiments with different reaction times.

Figure S 7: Temperature and pressure profiles obtained during liquefaction of wood. Autoclave: 9 mL; T: 320°C, Feed (w%); Guaiacol:Water:Wood = 60:20:20.

Figure S 8 shows the temperature and pressure profiles during liquefaction at different water concentrations. The temporary dip in the temperature profile is not observed in absence of water and in the presence of 10 w% water, while in the presence of 20 w% of water, a clear decrease in the temperature is observed as mentioned earlier also. Possibly with 10 w% water, the boiling of water and/or reaction is slower, and the heat consumption is spread over a longer time and becomes unnoticeable.

Figure S 8: Temperature (a) and pressure (b) profiles obtained during the liquefaction of wood with different water concentrations. Autoclave: 9 mL; T: 320°C, Feed (w%); Guaiacol:Wood:Water = (80-X):20:X.

For 10 w% and 20 w% of water concentrations, the pressure profiles are almost the same except the region where boiling of water and/or reactions are believed to be occurring that leads to decrease in temperature. With no water there is no sharp increase in the pressure, suggesting that the sharp increase in the pressure is due to release of water. The maximum pressure in presence of water is 9.3 MPa while in absence of water it is 5.0 MPa. Partial pressure of guaiacol at 320°C could be in between 0.6 to 0.8 MPa depending upon the water concentration in the feed.

Chapter 4

Liquefaction of lignocellulose: Do basic and acidic additives help out?

1. Screening of various homogeneous additives

As shown in Figure S 1, mainly CO_2 and CO were produced during the liquefaction of wood using various additives.

Figure S 1: Yields of different gases produced during liquefaction with different additives. Hydrogen yield is calculated based on hydrogen present in the feed wood. Autoclave: 9 mL; T : 320°C ; τ : 400 s; Feed (w%); Guaiacol:Wood:Water = 60:20:20.

Figure S 2 shows the apparent molecular weight distributions of the organic liquid effluents obtained after the liquefaction of wood using the various additives. Acid produces more heavies while base additives show a reduction in the heavies compared to the no additive liquefaction. A high additive concentration is resulted in a larger reduction in the heavies.

Figure S 2: Apparent molecular weight distributions of the organic liquid effluents obtained after liquefaction of wood using different additives with concentration (a) 1 w% and (b) 5 w%. Autoclave: 9 mL; T : 320°C, τ : 400 s; Feed (w%); Guaiacol:Wood:Water = 60:20:20 (excluding additives amount).

TAN (Total acid number) of the organic liquid effluents was measured, using the method described by Oasmaa et. al.²³. The measured TAN was further converted on wood basis by dividing it with the wood concentration of the feed. Table S 1 shows the TAN (mg of KOH/g of wood) of the organic liquid effluents (product), and pH of the feeds (without wood) and the organic liquid effluents. The pH of the organic liquid effluent obtained with the strong acid shows increase in pH from feed to the product (1.4 to 2.8) while with the strong base (1 w%) it shows decrease in pH (10.1 to 5.5). Such increase and decrease in pH when liquefying wood to organic liquid effluent, shows the buffering power of the wood, that is neutralization

of excessive acid by the minerals of the wood (as well as the wall of the reactor) and neutralization of excessive base by the conversion of sugar to carboxylic acids.

Table S 1: Detailed experimental and analyzed data. Autoclave: 9 mL; T: 320°C, τ : 400 s, Feed (w%); Guaiacol:Wood:Water = 60:20:20 (excluding additive).

		Yield (C%)				VR fraction	TAN (mg of KOH/g of wood)	pH		Elemental analysis of solid			
									Organic liquid effluent	Feed ^a	C H O*		
Additive (w%)		Liquid	Gas	Solid									
No cat		91.9	6.9	1.2	0.33	66	3.6	4.4	49.2	6.2	44.6		
H ₂ SO ₄	1	95.9	3.5	0.6	0.43	61	2.8	1.4	49.2 ^b				
CH ₃ COONa	1	92.0	7.7	0.3	0.31	118, 111	4.9	7.2	49.2 ^b				
CH ₃ COONa	5	91.2	8.0	0.8	0.23	90	5.7	7.7	49.2 ^b				
CH ₃ COOK	1	91.2	7.3	1.5	0.27	59, 58	5.4	7.7	46.3	9.6	44.1		
CH ₃ COOK	5	87.9	7.3	4.7	0.20	46	6.2	7.7	45.6	9.4	45.1		
KHCO ₃	1	90.5	8.0	1.5	0.26	38	5.5	8.5	43.7	5.4	50.8		
KHCO ₃	5	89.6	10.3	0.1	0.14	11	7.3	8.6	49.2 ^b				
KOH	1	90.8	6.9	2.3	0.23	30, 48	5.5	10.1	49.2 ^b				
KOH	5	76.3	7.0	16.7	0.10	0	9.13	10.1	36.2	3.1			

^aby difference, possibly small amount of salts also present; ^aexcluding wood; ^bassumed to be same as the carbon content of the solid obtained in case of no additive.

TAN measurements were typically determined at final titration pH of around 9.0-9.8. TAN of the organic liquid effluent without any additive is similar to the TAN of pyrolysis oil, namely around 70²³. It seems that CH₃COONa is catalyzing the formation of acidic compounds and producing an organic liquid effluent with the highest TAN. The low TAN in case of KHCO₃ is possibly due to its decomposition into KOH and CO₂, and the KOH is neutralizing the produced acids (e.g. forming acetate). This is also in line with the low TAN of the organic liquid effluent obtained with KOH. The high pH of the organic liquid effluent produced with 5 w% of KOH shows that the 5 w% of KOH was sufficient to neutralize all the acids formed during the liquefaction.

Table S 2: Characteristics of guaiacol and the organic liquid effluents obtained after liquefaction of pine wood using different acid and base additives. Autoclave: 9 mL; T: 320°C, τ : 400 s, Feed (w%); Guaiacol:Wood:Water = 60:20:20 (excluding catalyst amount).

	Additive (w%)	Water (w%)	HHV (wet, MJ/kg)	HHV (dry, MJ/kg)	EA (dry, w%)				H/C _{eff} ^b
					C	H	O ^a	N	
No cat	0	6.1	27.1	28.9	65.5	6.6	27.3	0.5	0.59
H ₂ SO ₄	1	7.6	26.4	28.6	67.8	6.4	25.2	0.6	0.58
KOH	5	6.4	26.5	28.4	59.7	6.7	33.0	0.5	0.53
KHCO ₃	5	7.5	26.3	28.4	60.8	6.9	31.8	0.5	0.58
CH ₃ COOK	5	14.1	25.1	29.2	61.2	6.7	31.6	0.6	0.54
CH ₃ COONa	5	7.0	26.5	28.5	66.3	6.8	26.3	0.5	0.64
KOH	1	6.8	26.8	28.7	66.3	6.6	26.6	0.5	0.59
KHCO ₃	1	7.3	26.4	28.5	66.8	6.9	25.8	0.6	0.65
CH ₃ COOK	1	6.7	26.7	28.7	66.3	6.8	26.4	0.5	0.63
CH ₃ COONa	1	6.1	26.7	28.4	66.4	6.6	26.4	0.5	0.60
Guaiacol	0	0.0	28.9	28.9	67.7	6.5	25.8	0.0	0.57

^adetermined by difference, ^bH/C_{eff} = (H-2×O)/C where H, O and C are moles of hydrogen, oxygen and carbon.

Properties such as HHV (higher heating value), moisture content, elemental composition and H/C_{eff}²⁴ of the organic liquid effluents vary slightly (Table S 2). The moisture content lies in between 6-8 w% with one exception of CH₃COOK (5 w%), possibly due to sampling errors. Considering the similar product yields obtained in all the runs, similar values of HHV and elemental composition of the organic liquid effluents were expected. HHV and elemental composition of the organic liquid effluents are similar to guaiacol which was also expected as majority of the organic liquid effluents consist of guaiacol.

2. Refill experiments

Detailed experimental data and analyzed data in the refill experiments with KHCO₃ are shown in Table S 3.

Table S 3: Detailed experimental and analyzed data in refill experiments. Base: 5 w% KHCO_3 , Autoclave: 45 mL; T : 320°C, τ : 30 min, Feed (w%); Guaiacol:Wood:Water = 65:20:10.

Sample	Yield (C%)			VR fraction	Elemental analysis of solid (w%)		
	Liquid ^a	Gas	Solid		C	H	O ^b
Single run	87.4	8.7	3.9	0.08	51.0	6.8	42.2
Refill of wood + KHCO_3	7.9	12.8	79.3	0.23	71.4	3.9	24.7
Refill of wood	44.4	8.2	47.3	0.26	72.6	3.9	23.5
Refill of KHCO_3	61.2	17.5	21.3	0.10	63.2	3.4	33.4

^adetermined as 100-gas-solid, ^bby difference.

GC-MS analysis of the organic liquid effluents obtained after the liquefaction of wood in the blank run as well as with KHCO_3 (Figure S 3) show decomposition of guaiacol, mainly into 1,2-Dimethoxybenzene. Other GCMS detectable compounds were present in very low concentration, and it was difficult to distinguish between compounds derived from wood and compounds derived from guaiacol.

Figure S 3: GCMS of the organic liquid effluents obtained (a) with 5 w% KHCO_3 , Autoclave: 45 mL; T : 320°C, τ : 30 min; Feed (w%); Guaiacol:Wood:Water = 65:20:10; (b) in blank run, KHCO_3 (5 w% of the total feed) and Guaiacol only, Autoclave: 9 mL; T : 320°C, τ : 400 s.

3. Quantifying the liquid yields

The liquid yields in the refill experiments determined gravimetrically appeared to decrease upon refill while the GPC curves showed a build-up of the bio-crude ($M_{w, \text{GPC}} > 180 \text{ Da}$) upon refill. This may suggest that the start-up solvent (Guaiacol) is possibly decomposing into bio-crude and char in the presence of a base. To understand this discrepancy in the liquid yield and the GPC data, quantification of the bio-crude (and the VR) was done using the GPC data and proper calibration with a bio-crude sample.

Figure S 4 shows the cumulative mass of all the products, and the VR in the organic liquid effluents obtained after the refill experiments versus the cumulative wood loading. The bio-crude and the VR yields were calculated using the GPC curve (by calculating GPC area) while solid and gas yields were calculated gravimetrically. The slopes of the curves shown in Figure S 4 give the average yields.

Figure S 4: Cumulative mass of carbon in the bio-crude, solid, gas and VR versus the cumulative mass of carbon in the wood (a) during the refill of wood only (KHCO_3 was used only in the first run) and (b) during the refill of wood as well as KHCO_3 . Mass (of carbon) of the liquid and VR were calculated using GPC curve while mass (of carbon) of solid and gas were calculated gravimetrically. Trend lines are the linear fits passing through the origin. Autoclave: 45 mL; T: 320°C, τ : 30 min, Feed (w%); Guaiacol:Wood:Water = 65:20:5. Additive loading: KHCO_3 , 5 w%.

Figure S 5 shows the solvent amounts that should be in the organic liquid effluents in case there is no solvent degradation, versus the solvent amounts calculated using the GPC curves (area of guaiacol peak at ~100 Da) and using the response factor of guaiacol. It clearly shows a pronounced decrease in the solvent concentration in the organic liquid effluent upon successive refill. Around 40 w% of the solvent was missing at the end of the refill experiment.

Figure S 5: Mass of the solvent (guaiacol) that should be in the organic liquid effluent in case of no decomposition of the solvent, and mass of the solvent calculated using GPC, during the refill of wood only (KHCO_3 was used only in the first run). Autoclave: 45 mL; T : 320°C, τ : 30 min, Feed (w%); Guaiacol:Wood:Water = 65:20:5, Additive loading: KHCO_3 , 5 w%.

4. Solid characterization

Figure S 6 shows the FT-IR spectra of the solid residues obtained after the liquefactions. Because of experimental artefacts such as sample packing, differences in band intensities between spectra should not be taken as indication for differences in concentration of the corresponding functional group between the samples. The wood structure is dominated by carbohydrate bonds C-O (1030 cm^{-1})/C-H (2900 cm^{-1})/O-H (3330 cm^{-1}) and some aromatic structure of lignin (1590 and 1505 cm^{-1}). The FT-IR spectrum of the solid residue obtained after the liquefaction with KHCO_3 clearly shows that the solid is char (mainly dominated by aromatic bands) and not unconverted wood. This char is quite similar to the char obtained through the blank experiment i.e. only with KHCO_3 , guaiacol and water but without wood.

Figure S 6: FT-IR spectra of residue constituents after the liquefaction runs. Autoclave: 45 mL; T : 320°C, τ : 30 min.

Chapter 5

Liquid upgrading: A two stage process concept for direct liquefaction of biomass

1. Detailed experimental data and gas analysis

The detailed experimental data and results of the refill experiments with intermediate hydrotreatment using Ru/C (5 w%) are provided in Table S 1. The removal of the condensates controlled the reactor pressure to be in between 70-90 bar. The product yields are similar (~80 w% liquid, ~12 w% gas and ~8 w% solid) in all the refill runs.

The gas compositions in the refill experiments are shown in Figure S1, which show that the gas phase is dominated by CO₂ and CO in the liquefaction runs while in the hydrotreatment runs it mainly contains unreacted H₂ with a small amount of methane.

Table S 1: Experimental conditions and results of the liquefaction runs 1 to 4 (R1-4) and the hydrotreatment runs 1 to 4 (T1-4). For the liquefaction; solvent:wood:water = 70:20:10 w%, T: 290°C, τ ~100 min; For the hydrotreatment; T: 210°C, τ : 120 min. Mass closure between 98-101 %.

Run	R1	T1	R2	T2	R3	T3	R4	T4
Solvent (g)	174.4	235	196.5	266.4	215.1	292.2	179	241.8
Fresh wood + water (g)	49+25		56+28		62+30		51+25	
Cumulative wood (w%)	21.9	n.a.	39.2	n.a.	52.5	n.a.	63.3	n.a.
Maximum P (bar)	74.2	185	92.3	190	92.3	200	74.1	189
Absolute yield (based on total feed)								
Yield Gas (w%)	1.8	0.7	1.9	0.2	1.9	0.6	2.1	0.3
Yield Condensates (w%)		14.9		13.6		33.9		22.6
Yield Char (w%)*		1.3		1.8		2.1		1.2
Yield Oil (w%)	96.6 ^a	84.8	96.3	83.1	96.4	62.6	96.7	75.3
H ₂ consumption (g)		11.6		5.10		3.0		1.9
Combined yield based on fresh wood**								
Yield Condensates + Oil (w%) ^b	81.3		81.2		77.8		82.5	
Yield Char (w%)	6.3		8.8		10.1		5.5	
Yield gas (w%)	12.4		10.0		12.1		12.0	
Organic liquid effluent analysis								
Solvent (%) (M _{w, GPC} < 180 Da)	80.7	68.0	52.9	50.7	40.1	34.9	28.0	23.9
Bio-crude (%) (M _{w, GPC} > 180 Da)	19.3	32.0	47.1	49.3	59.9	65.1	72.0	76.1
Viscosity (cP at 30°C)	17.6	21.6	26.4	39.6	57.2	866	360	3400
Water in the oil (w%)	13.3	6.4	18.7	11.6	22.5	1.4	14.9	1.1

n.a. : not available; *calculated as total solid obtained-catalyst intake; ** based on the wood intake in the liquefaction run; ^aYield of oil in runs R1-4 also include char. A duplicate run of R1 under same conditions gave very low char yield 0.7 w% on wood intake; ^bCondensates + oil yield was calculated as 100%-gas-%char.

Figure S1: Composition of the gas phase obtained in the refill experiments with intermediate hydrotreatment. For the liquefaction; solvent:wood:water = 70:20:10 w%, T : 290 °C, τ ~100 min, For the hydrotreatment T : 210 °C, H_2 pressure: 190 bar, τ : 120 min, Catalyst: 5 w% of Ru/C (5 w%).

Chapter 6

Fractionation of organic liquid effluent by temperature-swing extraction: Principle and application

1. Product definition and calculation

These definitions are reproduction of the definitions used in the main book.

Distillates: Oil molecules with molar mass $M_{W, GPC} < 1000$ Da. ‘Distillates’ also includes the starting liquefaction solvent ($M_{W, GPC} < 180$ Da).

Light oil: Light(er) oil, used as a liquefaction medium.

Heavy oil: Heavy oil obtained after removal of the light oil from the organic liquid effluent.

Vacuum residue (VR) fraction: Fraction of a liquid (organic liquid effluent, light oil or raffinate/heavy oil) that is found in the vacuum residue ($M_{W, GPC} > 1000$ Da) based on equation S.1. Here also the VR fraction is defined as a fraction of the organic liquid effluent rather than a fraction of the bio-crude i.e. excluding the starting solvent, as defined until now.

$$\text{Vacuum residue(VR) fraction} = \frac{\text{Area corresponds to } M_{W, GPC} > 1000 \text{ Da}}{\text{Total GPC Area}} \quad (\text{S.1})$$

Extracted percentage: Percentage of the feed (organic liquid effluent) that is extracted by the extraction solvent and found in the extract, as defined in equation S.2.

$$\text{Extracted percentage} = \left(1 - \frac{\text{Mass of raffinate}}{\text{Mass of organic liquid effluent}}\right) \times 100 \quad (\text{S.2})$$

Distribution coefficient: Concentration (g/g) ratio of the distillates (solute) in the extract and in the raffinate (equation S.3).

$$\text{Distribution coefficient} = \frac{\text{Distillates concentration in extract (g/g)}}{\text{Distillates concentration in raffinate (g/g)}} \quad (\text{S.3})$$

Minimum miscibility temperature: Minimum temperature above which a liquid mixture of a given composition is miscible.

Hansen solubility distance (Ra): It is the overall difference in solubility parameters of two molecules, typically solute and solvent, defined in the Hansen parameters space according to equation S.4. Here δ_{Di} , δ_{Pi} and δ_{Hi} are the three Hansen solubility parameters that are related to dispersion forces, dipole forces and hydrogen bonding respectively²⁵.

$$Ra^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (\text{S.4})$$

2. Distillation

Distillation was used to recover the light oil to be used as a liquefaction medium. Distillation was first carried out at atmospheric pressure and then under vacuum, in a laboratory batch distillation unit (made of glass). An electrical heater was used to heat the distillation flask and an electrical pump was used to create vacuum.

Distillation conditions and the distillation results are shown in Table S1. The boiling point of guaiacol at various pressures was obtained experimentally, and plotted in Figure S 2. A straight line nicely fits the experimental boiling point data of guaiacol which was used to translate the boiling points of the organic liquid effluent components under vacuum to boiling points at atmospheric pressure.

True boiling point curve of the organic liquid effluent is shown in Figure S1. Boiling points at vacuum conditions were converted to atmospheric boiling points using the correlation (equation S.5) which applies to guaiacol as determined experimentally (Figure S 2).

$$T_2 = T_1 + 29 \times \ln\left(\frac{P_2}{P_1}\right) \quad (\text{S.5})$$

Here T_i is boiling point ($^{\circ}\text{C}$) at pressure P_i (bar).

Distillate 1 (4 w%) and 2 (6 w%) were obtained under atmospheric pressure while distillate 3 (52 w%) and distillate 4 (10 w%) were obtained at 4 mbar.

Table S1: Distillation conditions and results. Feed composition used in the liquefaction reaction through which the organic liquid effluent (feed to distillation) was obtained: Guaiacol:Wood:Water = 85:10:5 w%. In the bracket shows boiling temperature corresponding to atmospheric pressure, and the amount distilled as a percentage of the feed to distillation.

Feed to distillation column			
	Mass	453.09	g
	Density	1.20	g/ml
Atmospheric distillation			
	Pressure	1.0124	bar
	Initial temp	14	°C
Atm. Distillate-1 (0-99°C, 4 w%)	Mass	20.1	g
	Density	0.98	g/ml
	Top temp	99	°C
	Bottom temp	137	°C
Atm. Distillate-2 (99°C -105°C, 6 w%)	Mass	26.1	g
	Density	1.21	g/ml
	Top temp	105	°C
	Bottom temp	207	°C
Vacuum distillation			
	Pressure	0.004	bar
	Initial temp	14	°C
Vacuum. Distillate-1 (about 105-220°C at 1 atm, 52 w%)	Mass	236.05	G
	Density	1.17	g/ml
	Top temp	85	°C
	Bottom temp	115	°C
Vacuum. Distillate-2 (about 220-320°C at 1 atm, 10 w%)	Mass	45.75	g
	Density	N/A	g/ml
	Top temp	167	°C
	Bottom temp	325	°C
Condensate (3 w%, collected in the ice bath)			
	Mass	8.98	g
Distillation residue (20 w%)	Mass	92.01	g
Total mass recovered (95 w%)		428.96	g
Unrecovered Mass (5 w%)		24.13	g

Figure S 1: True boiling point curve of the organic liquid effluent. The vacuum boiling points (4 mbar) are reported between the brackets. Vertical lines show various distillation cuts (1-4).

In summary, distillation is effective in recovering the light oil. Around 80 % of the feed was obtained as distillate (including the 3 % condensate and the 5 % unrecovered mass) which is around 90 % of the total liquefaction solvent used (guaiacol + water) during the liquefaction reaction. The liquefaction solvent recovery was insufficient here but may be improved by applying a higher distillation temperature.

Figure S 2: Boiling point of guaiacol as a function of pressure (bar).

3. Extraction

3.1. Solvent screening

Organic compounds with moderate polarity, that is with an octanol-water partition coefficient $\log P < 3.9$, form a single phase with guaiacol ($\log P$: 1.3) at room temperature (Table S 2). In contrast, compounds with low polarity, that is $\log P > 3.9$, are immiscible with guaiacol at room temperature but become miscible at high temperature. Interestingly, very polar media such as water and water/methanol mixtures were also immiscible at low temperature and miscible at high temperature.

Hansen parameters of water/methanol mixture were defined as the volume average of Hansen parameters of water and methanol.

Table S 2: Screening of solvents: Extraction test results with guaiacol. “X” indicates no phase transition i.e. transition from two phases to a single phase or vice-versa.

Compound	log P (VCCl ab) ²⁶	log P (Sangster) ²⁷	Transit- ion at (°C)	Hildebrand parameter ²⁸	Hansen parameters ²⁸ ([J/ml] ^{0.5})			Ra* ([J/ml] ^{0.5})
					δ_s	δ_p	δ_h	
Water			180	47.8	15.5	16	42.3	30.4
Water/methanol 60/40			40	40.5	15.3	14.52	34.3	22.6
Water/methanol 50/50			5	38.7	15.3	14.15	32.3	20.6
Glycerol	-1.58	-1.74	X	36.1	17.2	12.1	29.3	16.5
Methanol	-0.59	-0.74	X	29.6	15.1	12.3	22.3	11.5
Acetic acid	-0.13	-0.17	X	21.4	14.5	8	13.5	7.0
Ethanol	-0.07	-0.30	X	26.5	15.8	8.8	19.4	7.5
Furfural	0.53	0.46	X	24.4	18.6	14.9	5.1	10.7
n-butanol	0.93	0.84	X	23.2	16	5.7	15.8	5.3
Diethyl ether	0.97	0.89	X	15.6	14.5	2.9	5.1	12.0
Guaiacol	1.41	1.32	X	23.5	18	8.2	13.3	0.0
Toluene	2.50	2.73	X	18.2	18	1.4	2	13.2
Ethylbenzene	2.96	3.15	X	17.9	17.8	0.6	1.4	14.1
1-octanol	3.05	3.07	X	20.6	16	5	11.9	5.3
Cyclohexane	3.12	3.44	11	16.8	16.8	0	0.2	15.6
Hexane	3.55	3.90	41	14.9	14.9	0	0	16.8
1-methylnaphtalene	3.63	3.87	X	21.1	20.6	0.8	4.7	12.5
Heptane	4.00	4.66	47	15.3	15.3	0	0	16.5
Octane	4.36	5.15	48	15.5	15.5	0	0	16.4
Undecane	5.52	6.54	54	16.0	16	0	0	16.1
Dodecane	5.99	6.10	58	16.0	16	0	0	16.1
Hexadecane	7.83		67	16.3	16.3	0	0	16.0

*Hansen solubility distance from guaiacol

Ideal operating line for extraction:

$$M_{\text{organic liquid effluent}} = M_{\text{Extracted oil}} + M_{\text{Raffinate}} \quad (\text{S.6})$$

$$M_{VR,O} = M_{VR,E} + M_{VR,R} \quad (\text{S.7})$$

$$VR, O = \frac{M_{VR,O}}{M_{Organic\ liquid\ effluent}} \quad (S.8)$$

$$VR, R = \frac{M_{VR,R}}{M_{Raffinate}} \quad (S.9)$$

$$VR, E = \frac{M_{VR,E}}{M_{Extract}} \quad (S.10)$$

Here, M_i is mass of component 'i'; VR,O , VR,R and VR,E are vacuum residue fraction of the Organic liquid effluent (O), Raffinate (R) and Extracted (E) oil respectively.

$$Extracted \% (Ex) = \left(1 - \frac{M_{Raffinate}}{M_{Organic\ liquid\ effluent}}\right) \times 100 \quad (S.11)$$

For the ideal condition, the entire vacuum residue should land in the raffinate, $\therefore VR,E = 0 \Rightarrow M_{VR,E} = 0$

$$\therefore M_{VR,O} = M_{VR,R} \text{ (from equation S.7)} \quad (S.12)$$

Combining equations (S.8), (S.9), (S.11) and (S.12):-

$$VR, R = \frac{100 \times VR, O}{100 - Ex} \quad (S.13)$$

Equation S.13 is equation for the ideal operating line.

Calculation of Extracted percentage based on GPC:

Extracted percentage based on GPC was calculated using equations S.6-S.11. Here VR,R , VR,O and VR,E are calculated using the GPC curves, mass of the organic liquid effluent feed can be taken any value. So there are 6 unknowns and 6 equations which give an unique solution.

3.2. Multistage extraction

Figure S 3 shows schematic of experimental procedure of multistage extraction.

Figure S 3: Experimental procedure of multi-stage extraction with intermediate solvent (extraction) recovery. Light oil: L, Heavy oil: H, Solvent: S.

Figure S 4 shows GPC curves of various streams obtained in the multistage extraction which illustrates no significant change in the extraction solvent as well as in the recovered light oil with number of stages.

Figure S 4: Apparent molecular weight distributions of (a) raffinates (Hot reject: R1-R-4; full line), light oils (cold reject: 1-4; dotted lines), organic liquid effluent, regenerated solvent in stage 4 and (b) regenerated extraction solvent: 1,2,4. Extraction T: 70°C, Recovery T: 25°C. Stages: 1-4.

4. General application: Fractionation of petroleum crude oil

The extraction experiments consisted of a few consecutive extractions at 50°C or 60°C using about 5 g of fresh basra crude oil and about 16 g of extraction solvent. The extraction was followed by solvent regeneration by cooling at room temperature and allowing for Liquid/Liquid demixing using a centrifuge. The solvent consists of fresh n-Butanol for the

first run (Run-1) and recycled solvent for the subsequent runs (Run-2 and Run 3). Fresh basra crude oil was used in each run. n-Butanol was used as an extraction solvent because it has a Hansen solubility distance (Ra) of 16.1 from the crude oil. Solvents with a larger Hansen solubility distance (e.g. Methanol with Ra: 25) indeed did not extract any component from the crude oil while solvents with a smaller Hansen solubility distance (e.g. n-Octanol with Ra: 12.3) dissolved almost all the crude oil. The detailed experimental conditions and results are provided in Table S 3.

Table S 3: Detailed Experimental data. Solvent: n-Butanol. Amount of n-Butanol in various streams was measured by GC-MS. frac.: fraction, rec: recovered, Ext.: Extraction.

		Run-1	Run-2	Run-3	Run-1	Run-2
Ext. Temp		60°C			50°C	
Basra (g)		5.1	5.1	5.0	5.0	5.1
Solvent (g)		16.1	16.3	15.5	16.2	17.2
Extracted oil	Mass (g)*	2.3 (45%)	3.2 (63%)	4.3 (86%)	1.0 (20%)	2.3 (45%)
	Mass (butanol free)	2.1 (41%)	2.7 (54%)	3.6 (72%)	0.9 (18%)	2.0 (40%)
	Butanol %	10.5	13.7	16.1	9.2	11.4
	VR frac.**	0.50	0.42	0.39	0.46	0.40
Raffinate	Mass*	1.4 (27%)	1.9 (37%)	1.7 (34%)	2.8 (56%)	2.7 (53%)
	Mass (butanol free)	1.2 (23%)	1.6 (31%)	1.4 (28%)	2.4 (47%)	2.3 (46%)
	Butanol %	13.3	16.6	14.0	15.5	14.4
	VR frac.	0.65	0.61	0.60	0.62	0.56
Solvent rec.	Mass	17.1	16.1	14.5	17.2	17.1
	Mass (butanol free)	1.8 (35%)	1.5 (29%)	1.4 (29%)	-	0.6 (13%)
	Butanol %	89.4	90.4	90.1	-	96
	VR frac.	0.17	0.19	0.18	-	0.18

**Percentage is calculated based on basra crude oil amount; **VR fraction of basra crude oil is 0.41*

Figure S 5 shows the VR fraction in the raffinate and in the extracted oil versus raffinate percentage at 60°C. Accordingly, the 60°C fractionation produced about 35 % of raffinate with a VR fraction of ~0.6. The extracted oil was not clearly enriched in lighter product with the current molar mass cutoff for the VR of 1000 Da. However when the cutoff was increased (e.g. 4000 Da), a clear enrichment of lighter product could be seen (reduction of VR from 0.1

in the crude oil to 0.04 in the extracted oil). When carried out at 50°C, however, the fractionation produced slightly more raffinate (around 50 %) with a marginally lower VR fraction (0.56 for run-2). The regenerated solvent in the extraction at 50°C showed no difference compared to the regenerated solvent in the extraction at 60°C, which was expected as regeneration temperature was same in both the cases.

Figure S 5: VR fraction in the raffinate and in the extracted oil versus raffinate percentage (mass of raffinate/mass of crude oil $\times$ 100) obtained in the three runs. Between the brackets shows the run number. Extraction solvent: *n*-Butanol (3.2:1 weight ratio), Extraction T: 60°C, Recovery T: 25°C. VR fraction in the crude oil: 0.41.

GPC analysis of the various extraction streams (extraction T: 60°C) are shown in Figure S 6a which shows that the crude oil is being split into two fractions, namely a light fraction (extract) and a heavy fraction (raffinate). The solvent contained a small amount of light components in order to reach a saturation point as expected. Further carrying out extraction with the regenerated solvent hardly shows any significant difference compared to the pure solvent. A slight different GPC profile of the Ext-1 liquid compared to the other two (Ext-2 and Ext-3) is possibly caused by experimental errors occurred during separation of the two phases. The separation is based on the molar mass, and is not selective to aromatic or aliphatic components as the UV signal also showed similar profiles as the RID signal.

Similar results were also obtained when extraction temperature was lowered to 50°C (Figure S 6b).

Figure S 6: Apparent molecular weight distributions of different extraction streams (Basra crude oil, Raffinate (Ra.), Extract (Ex.) and regenerated solvent (Sol.)). Solvent: *n*-Butanol, Solvent/Feed ~3.2 weight ratio, Extraction at (a) T : 60°C, regeneration T : 25°C. (b) T : 50°C, regeneration T : 25°C.

5. Discussion: Theory of fractionation

Derivation of ϕ_2^{max}

Here $\phi_2 = \phi_2^{max}$

$$\phi_2 = -\frac{1}{\chi_{12}} \left(\ln \phi_1 + \frac{\phi_2 \rho_2}{\phi_1 \rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2 \right) = -\frac{1}{\chi_{12}} \left(\ln(1 - \phi_2) + \frac{\phi_2 \rho_2}{\phi_1 \rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2 \right)$$

$$\ln(1 - \phi_2) = \ln(1 + (-\phi_2)) = (-\phi_2) - \frac{1}{2}(-\phi_2)^2 + \frac{1}{3}(-\phi_2)^3 - \frac{1}{4}(-\phi_2)^4 + \dots$$

For a dilute solution, $\phi_1 \sim 1$ and $\phi_2 \ll 1$

$$\ln(1 - \phi_2) \sim -\phi_2$$

$$\phi_2 = -\frac{1}{\chi_{12}} \left(-\phi_2 + \frac{\phi_2 \rho_2}{\rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2 \right) = \frac{\phi_2}{\chi_{12}} \left(1 - \frac{\rho_2}{\rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2 \right)$$

$$\chi_{12} = \left(1 - \frac{\rho_2}{\rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2 \right)$$

$$\chi_{12} - 1 = -\frac{\rho_2}{\rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2$$

$$-(\chi_{12} - 1) = \frac{\rho_2}{\rho_1} \frac{M_{W1}}{M_{W2}} \ln \phi_2$$

$$\phi_2 = e^{-\frac{M_{W2}}{M_{W1}} \frac{\rho_1}{\rho_2} (\chi_{12} - 1)}$$

This simplification shows the same results compared to the original equation at low volume fraction of the organic liquid effluent considered as polymer, as shown in Figure S 7.

Figure S 7: Volume fraction of the organic liquid effluent in hexadecane solvent versus the molar mass of the organic liquid effluent calculated using the model. Dotted line shows results obtained after simplification of the model.

6. Process simulation for fractionation of the organic liquid effluent

In both schemes (Distillation and extraction), the lignocellulosic feed is liquefied in a liquefaction reactor. The reactor effluent is sent to a first separation unit that removes gases and water vapor (with small amount of light organic compounds) and then sent to a second separation unit that recovers the light oil for recycle to the liquefaction reactor, and produces a heavy oil product stream that can be sent to a refinery for further processing to biofuels. Depending on the process alternative, the second separation unit is either a distillation column or an extraction unit. In the latter case, the extract (containing the light oil) stream is sent to an extraction solvent recovery unit.

The product yield in the liquefaction reactor is taken from our experimental results, which showed liquid yield around 90 w%, gas yield 10 w% and negligible solid yield. For convenience, the solid yield was assumed to be zero. It was also found that around 25 w% water (based on the wood) was formed during the liquefaction. The amount of the ‘distillates’ ($M_{w, GPC} < 1000$ Da, includes guaiacol) in the organic liquid effluent was estimated from the VR fraction of the organic liquid effluent. The ‘distillates’ was modeled using guaiacol while the ‘heavies’ was modeled using Bisphenol-A. For convenience the light oil was assumed to be free from the ‘heavies’.

Calculation of extracted percentage required for closing the recycle:

Liquefaction Feed: (Solvent:Wood:Water = 55:30:15 w%)

Liquid yield (based on wood intake) = 90 w%

Water yield = 25 w% out of 90 w% of the liquid yield

Organic yield = $90 - 25 = 65$ %

Total water free liquid = Feed + Organic from wood = $55 + 30 \times 65/100 = 74.5$

Total feed to extraction = Total water free liquid = 74.5

Desired amount of the extract = Amount of the liquefaction solvent used = 55

Desired extracted % = $\text{Desired amount of the extract} / \text{Total feed to extraction} \times 100 = 55/74.5 \times 100 = 73.8$

As found in the distillation experiment, a high bottom temperature ($\sim 320^\circ\text{C}$) is used to recover sufficient amount of the light oil, and hence the heavy oil (product) is available at this temperature. However in the extraction, the raffinate (heavy oil) is available at a low temperature (70°C). For comparison of these two processes, the heavy oil needs to be made available at the same temperature. Since the heavy oil (bio-crude) is intended to be processed

in an FCC unit which requires feed at high temperature, therefore it was chosen to deliver the bio-crude at 320°C (bio-crude temperature in case of distillation).

Figure S 8 shows that the energy (heat duty) required to recover the light oil represents a significant fraction of the energy present in the feed wood at low wood loading (10 w%) but it readily becomes acceptable at and beyond 20 w% of wood loading. However high wood loadings may present challenges in solid feeding²⁹. The total heat transfer (including condenser) of the process follows the trend of the heat duty of the distillation column (Figure S 8).

Figure S 8: Heat duty and total heat transfer required to separate the light oil to recycle back versus the wood loading in the feed to the liquefaction reactor. Feed to the liquefaction: guaiacol:wood:water = (100-3X):2X:X w%. HHV: Higher heating value.

Material balance of the distillation process was calculated using the experimental yield data for wood loading varying between 10 and 40 w% while keeping the product yields unchanged. The column was operated at atmospheric pressure with a feed temperature of 208°C to keep it just in liquid phase (bottom T at 320°C). The light oil vapor was condensed at 205°C in order to pump it back to the liquefaction reactor.

A process flow sheet of the extraction process is shown in Figure S 9. Heating/cooling involved in the process are shown between the brackets in the figure. The solvent to feed ratio and the extracted percentage in each stage were kept as found experimentally and used for the material balance of the process. Firstly, heat available at high temperature ~208°C in the hot organic liquid effluent stream was used to heat the final raffinate stream which was further heated to 320°C using an additional heater unit. The cold stream of the extraction solvent

(Solvent, solvent-1) is heated using the hot extract stream and then mixed with the relatively hot raffinate stream.

Figure S 9: Extraction with water-methanol process flowsheet. Between the brackets shows heat duty (in MJ/ton of wood) of heat transfer equipment where '+', '-' and no sign indicate heating, cooling and heat exchange respectively. Minimum approach temperature was set at 10°C in a heat exchanger. Extraction T: 70°C, Recovery T: 25°C. Feed to liquefaction: guaiacol:wood:water = 55:30:15 w%.

The material balance around the liquefaction reactor is shown in Table S 4, which is same for both the process concepts. The ideal material balance of process streams of the two process concepts are provided in Table S 5 and Table S 6.

Table S 4: Material balance around the liquefaction reactor. T : 320°C, τ : 30 min. Feed: guaiacol:wood:water = 55:30:15 w%.

	Liquefaction reactor (ton/h)				
	Wood	Distillates	Water	Heavies	Off gases
Reactor-Feed	100	183	50	0	0
Reactor-out	0	213	75	35	10

Table S 5: Material balance of the distillation process.

Stream	Heavies	Distillates
(ton/h)		
Feed to dist.	35	213
Top product (light oil)	0	183
Bottom product (heavy oil)	35	30

Table S 6: Material balance of the extraction with water-methanol process.

	Stream	W+M	Heavies	Distillates
		(ton/h)		
Stage-1	Solvent	415	0	0
	Organic liquid effluent	0	35	213
	Ext-1a	415	0	114
	Raffinate-1	0	35	99
	Solvent-1	415	0	0
	Extract-1	0	0	114
Stage-2	Ext-2a	415	0	69
	Raffinate-2	0	35	30
	Solvent-2	415	0	0
	Extract-2	0	0	69

Table S 7: Estimated heat transfer duty and capital cost of various equipment. Plant capacity: 100 ton/h.

	Heat transfer duty (MW)	Cost (M\$, ISBL-2014)
Distillation		
Reboiler	24.9	27.3
Condenser	20.7	24.7
Extraction-Water/Methanol mixture		
Stage-1		
HE-0	4.8	11.0
HE-0-1	5.3	11.7
HE-1-1	10.9	17.3
HE-1-2	0.0	0.0
HE-1-3	12.5	18.7
Stage-2		
HE-2-1	16.3	21.6
HE-2-2	4.7	10.9
HE-2-3	6.1	12.6

Chapter 7

Liquefaction of lignocellulose in fractionated light oil: Proof of concept and techno-economic assessment

1. Liquefaction with intermediate separation

Detailed experimental data of liquid-liquid extraction are provided in Table S 1.

Table S 1: Detailed experimental data of the liquid-liquid extraction with hexadecane. Extraction T: 90°C, Regeneration T: 25°C. Ext.: Extraction.

	Stage	Ext. Solvent (g)	Feed (g)	Extracted oil (g)	Raffinate (g)	Unrecovered feed ^a (g)	Rejection ^b (w%)	Recovered ext. solvent (g)
Ext.-1	1	67.7	15.7	3.3	5.8		37	
	2			1.1	4.6	6.7		71.0
Ext.-2	1	69.5	15.0	4.0	7.9		53	
	2			3.1	6.1	1.8		69.5
Ext.-3	1	68.6	8.9	3.5	4.6		52	
	2			1.8	3.8	-0.2		66.6
Ext.-4	1	65.9	6.2	3.3	2.6		42	
	2			0.2	2.2	0.5		65.1
Ext.-5	1	17	4.0	1.5	1.7		42	
	2			0.1	1.4	1.0		16.5

^afeed-(final raffinate + total extracted oil), ^b(raffinate/feed) × 100 (w%)

Apparent molecular weight distributions of different streams obtained in series of liquefaction runs with intermittent solvent extraction and recycle are shown in Figure S 1. There is hardly any difference among the GPC profiles of the recovered solvents in all the extraction runs which indicates a stable solvent recovery process (1st peak is guaiacol and 2nd peak is hexadecane). The extracted oils (light oils) also do not show any significant difference in their molecular weight distributions. A slight increase in the heavies tail is observed in the organic liquid effluents as well as in the raffinates with refill runs. Notice that the raffinates and the extracted oils still contain some hexadecane as indicated by the peak at 300 Da. A deeper solvent recovery e.g. by distillation may be required.

Figure S 1: Apparent molecular weight distributions of (a) recovered extraction solvents (solvent 1-4), (b) extracted light oils after solvent recovery (Extract-1-5), (c) raffinates (raf-1-5) (d) liquefaction liquids (organic liquid effluents) fed to the extraction (Liq-1-5) and (e) liquefaction liquid (organic liquid effluent), extract, raffinate, solvent, in the 3rd extraction. Extraction T: 90°C, Recovery T: 25°C.

The VR fractions of the organic liquid effluents obtained after the refill experiments with and without intermediate separation were calculated using two ways namely including the liquefaction solvent and excluding the liquefaction solvent (Figure S 2). Inclusion of the liquefaction solvent in the calculation of the VR makes it dependent on the recycle. To exclude the effect of recycle, the VR fraction was further calculated excluding the liquefaction solvent which shows similar trend that is a steep increase in the VR fraction when

separation is not applied while a marginal increase in the VR fraction when intermediate separation is applied (Figure S 2).

Figure S 2: VR fraction versus cumulative wood (%) in the refill experiments with and without intermediate separation. VR fraction was calculated by two ways namely including the liquefaction solvent and excluding the liquefaction solvent. Liquefaction T : 320°C , τ : 30 min, Extraction T : 90°C , Recovery T : 25°C .

A constant gas composition was obtained during the liquefaction runs as shown in Figure S 3.

Figure S 3: Composition of the gas phase obtained after the liquefaction runs (with intermediate separation) with cumulative wood. Liquefaction T : 320°C , τ : 30 min.

Chemical functionalities of the raffinates were analyzed using FTIR and shown in Figure S 4 which hardly shows any difference among them.

Figure S 4: Normalized FTIR spectra of raffinates (1-5).

Organics and water yields calculation:

A mass balance and a carbon balance of the feed (wood only) and the products were used to calculate the amounts of the organics (bio-crude) and the water produced in the reaction.

Contaminations of the organics with the starting liquefaction solvent (guaiacol) and vice-versa were not considered in the calculation. However a small contamination would not have significant impact on the results as the starting liquefaction solvent has a similar elemental composition as of the organics (bio-crude). It was assumed that the liquefaction solvent does not produce gas or char. A blank experiment with only guaiacol and water but without wood showed marginal gas and no solid formation (Chapter 3 of the main book).

$$\text{Wood} \rightarrow \text{Organics} + \text{Water} + \text{Char} + \text{Gas} \quad (\text{r-1})$$

$$M_{\text{wood}} = M_{\text{organics}} + M_{\text{water}} + M_{\text{char}} + M_{\text{gas}} \quad (\text{S.1})$$

Here, M_i is mass of component 'i'. Two unknowns are M_{organics} and M_{water}

M_{organics} can be obtained from carbon balance:-

$$M_{\text{C,wood}} = M_{\text{C,organics}} + M_{\text{C,char}} + M_{\text{C,gas}} \quad (\text{S.2})$$

Here $M_{\text{c,i}}$ is mass of carbon in component 'i' which can be obtained using its elemental composition :-

$$M_{\text{wood}} \times C_{\text{wood (dry w\%)}} = M_{\text{organics}} \times C_{\text{organics (dry w\%)}} + M_{\text{char}} \times C_{\text{char (dry w\%)}} + M_{\text{gas}} \times C_{\text{gas (dry w\%)}} \quad (\text{S.3})$$

Here C_i (dry w%) is dry carbon weight % of component 'i' determined by elemental analyzer or in case of gas, using the gas composition.

Elemental compositions of all the constituents are known and hence M_{organics} can be obtained from equation S.3, and from equation S.1, M_{water} can be calculated. Elemental composition of the organics is taken as the elemental composition of the raffinate. Further checks were done for the rest elements oxygen and hydrogen which showed good match.

2. Process modeling and simulation

The process flow sheets of both the processes are shown in Figure S 5. In both the schemes, the feed mixture comprising wood, water and liquefaction solvent (light oil) is mixed and fed to the liquefaction reactor after heat exchange with the reactor effluent stream and finally heating it to the reaction temperature of 320°C. It has been assumed that around 5 w% of the reactor effluent will be present in the vapor phase. The reactor effluent is sent to a series of

heat exchanger and finally cooling it to room temperature and sending to a decanter where gas, organic liquid effluent and aqueous phase are separated out. However cooling the reactor effluent to room temperature may not be required for the phase separation; cooling to about 50-80°C possibly would be sufficient (not considered in this simulation). The organic liquid effluent was found to contain ~5 w% of water while aqueous phase is assumed to be pure.

Figure S 5: Process flow sheet of direct liquefaction of wood with separation of the light oil (a) using standalone distillation, and (b) using hybrid of extraction and distillation. In bracket shows heat duty (in GJ/ton of wood) of heat transfer equipment where '+', '-', and no sign indicate heating, cooling and heat exchange respectively. Minimum approach temperature was set at 10°C in a heat exchanger. Feed to liquefaction: guaiacol:wood:water = 55:30:15 w%.

In the first scheme, the obtained organic liquid effluent is sent to a flash column with a reboiler and a condenser after heating it through heat exchange with the reactor effluent, to recover enough light oil as the top stream, needed for recycling. In the bottom, the bio-crude

is obtained. The top stream is just condensed into liquid phase and recycled back as the liquefaction solvent.

In the second scheme the organic liquid effluent is first sent to an extraction unit to recover 55 w% of the organic liquid effluent as the light oil. The raffinate is processed in a finishing atmospheric flash column (bottom T: 320°C) to recover the remaining part of the light oil required to close the recycle loop. The extract is cooled to room temperature to recover the extraction solvent and recycle the light oil back to the liquefaction reactor.

Ideal material balance around the liquefaction reactor and the decanter are shown in Table S 2 and Table S 3 respectively which are same for both the processes. Material balance (ideal) of process streams of the two process concepts are provided in Table S 4 and Table S 5.

Table S 2: Material balance around liquefaction reactor. T: 320°C, time: 30 min.

	Liquefaction reactor				
	Wood	Distillates	Water (ton/h)	Heavies	Off gases
Reactor-Feed	100	183	50	0	0
Reactor effluent	0	211	80	28	14

Table S 3: Material balance around decanter.

Stream	Heavies	Distillates	Off gases	Water
			(ton/h)	
Reactor effluent	28	211	14	80
Organic liquid effluent	28	211	0	12
Off gases	0	0	14	0
Water*	0	0	0	68

*Recycle water: 38 ton/h; Excess water: 30 ton/h

Table S 4: Material balance around distillation column in scheme 1.

Stream	Heavies	Distillates	Off gases	Water
			(ton/h)	
Organic liquid effluent	28	211	0	12
Light oil	0	183	0	12
Bio-crude	28	28	0	0

Table S 5: Material balance around extraction and distillation in scheme 2.

Stream	Ext. Solvent	Heavies (ton/h)	Distillates	Water
Organic liquid effluent	0	28	211	12
Reg. Solvent	1005	0	0	0
Extract	1005	0	131	7
Raffinate	0	28	80	5
Light oil-1	0	0	131	7
Light oil-2	0	0	52	5
Bio-crude	0.0	28	28	0

3. Biomass feeding system

Feeding the liquefaction feed mixture in a high pressure reactor is critical for the process, and its cost has most likely not been properly captured by the capex-duty correlation used here; hence the need for dedicated consideration of biomass feeding system of a large feed stream of 330 ton/h ($\sim 330 \text{ m}^3/\text{h}$) at a relatively high pressure of 80-100 bar.

It has been reported in literature that a biomass slurry can be fed into a high pressure reactor using reciprocating pumps (e.g. piston, diaphragm or plunger pumps), which are popular for high pressure feeding³⁰⁻³². For the present process, piston pump seems the most suitable option. The operating range of a piston pump is very wide, with capacities ranging from 11 to 115 m^3/h , and feed pressures from 4.5 to 15 MPa³¹⁻³². Hence, three parallel feeders will be required to meet the capacity of the plant, although it might be wise to add a fourth pump as spare. The installed cost of the three piston pumps is estimated to be around 2 M\$ (for Duplex with steam driver)³³ to 3 M\$ (for solid feeder, Putzmeister KOS 2180)³⁴ in 2014 currency. The cost of feeding system with piston pump is 10-15 times higher than the cost of a feeding system consisting of 8 centrifugal pumps, each pump with a 10 bar head, installed in series^{30,33}. However the feasibility of such system is not proven at this moment.

Screw feeder and Lock-hopper are also used to feed the biomass, however their low capacity make them not suitable for this process³¹. An extruder-feeder reactor system was also reported to feed slurries as high as 60 w% of solid concentration into a 21 MPa pressure reactor³⁵. The process developed by PERC in the 80's used progressing cavity pumps for low pressure pumping and reciprocating plunger pumps with ball check valves for high pressure pumping³⁶.

4. Techno-economic assessment

The economic feasibility of the process was assessed using the procedure described in the book “Conceptual Design of Chemical Processes” by James M. Douglas and can be summarized below³⁷.

Assumptions

Start up	= 10 % of Fixed capital investment (FCI)
Working capital	= 15 % of FCI
Offsite costs	= 45 % of Onsite costs
SARE	= 25 % of total Revenue
Maintenance	= 4 % of FCI
Supply	= 15 % of maintenance cost
Supervision	= 20 % of labor cost
Lab	= 15 % of labor cost
Royalty	= 3 % of total production cost
Fixed charges	= 3 % of FCI
Depreciation	= 10 % of FCI
Owner's cost	= 5 % of direct costs
Contingency	= 20 % of direct costs
Utility costs	= Calculated based on burning wood
Labor costs	= 10 % of total production costs
Plant OVHD	= 60 % of Labor, supervision and maintenance costs

Based on above definitions and assumptions, following relations can be formulated:

Onsite capital = See duty-capex correlation (equation, S.4)

Direct cost = onsite + offsite = 1.45 onsite

Indirect cost = Owner's cost + contingency = 0.25 direct cost

Fixed capital = direct cost + indirect cost = 1.25 direct cost = 1.81 onsite

Total investment = fixed capital + working capital + startup = 1.25 fixed capital = **2.26 onsite**

Total Production cost = Manufacture cost + SARE

SARE ~ 0.025 (Revenue)

Manu. Cost = Direct prod. Cost + Fixed charges + plant OVHD

Direct prod. cost = Raw matl. + Utility + Maintenance + Op. Supply + labor + supervision +
Laboratory + Royalty

Maintenance = 0.04 fixed capital

Supply = 0.15 maintenance = 0.15×0.04 fixed capital

Supervision = 0.2 labor

Lab = 0.15 labor

Royalty = 0.03 total prod. cost

Direct Prod. Cost = Raw Matl. + Utility + 0.046 (FCI) + 1.35 (labor) + 0.03 (tot prod. cost)

Fixed charges = Tax + insurance + rent + interest + Capital cost charges (due to investment)

Tax + insurance = 0.03 fixed capital

Interest = 0; i.e. 100 % equity financed

Rent = 0

Capital charge is derived with the annuity method employing a 10 % interest rate and a service life of 20 years as given by below equation.

Capital cost charge = Capital Recovery Factor $\times$ Total investment

Capital Recovery Factor = $i(1+i)^n / ((1+i)^n - 1)$; here i = interest rate, n = service life of the project

Fixed charges = 0.03 Fixed cap. + Capital cost charges

Plant OVHD = 0.6 (Labor + supervision + maintenance)

= 0.72 Labor + 0.024 Fixed Cap.

Total Prod. Cost = Direct prod. + Fixed chg. + Plant OVHD + 0.025 Revenue

= 1.03 (raw matl. + Utility) + 2.13 labor + 0.103 Fixed cap. + 0.025
Revenue + Capital cost charges

In this study the onsite cost was calculated using the correlation suggested by Lange³⁸ as given by equation S.4, which is corrected for the investment cost for the year 2014 by replacing the original factor of 2.9 with 4.7 to account for cost escalation from year 1993 to 2014. Rest of the calculations was done based on the procedures mentioned above.

$$\text{Onsite cost [M\$ 2014]} = 4.66 \times (\text{energy transfer [MW]})^{0.55} \quad (\text{S.4})$$

The detail of process economics data of the two process concepts are provided in Table S 6.

Table S 6: Process economics data of the two process concepts. Operation hours: 8320 h/year.

		Distillation	Extraction
Plant capacity	kt/year of dry wood	800	
Feed	ton of dry wood/h	100	
Product	ton of bio-crude/h	56	
Feed price	\$/ton of wood	85	
Onsite cost	M\$	165	173
Total investment	M\$	375	393
Fixed Capital	M\$	299	314
Working	M\$	56	59
Start up	M\$	30	31
Raw materials	M\$/year	71	71
Energy cost	M\$/year	8	5
Labor	M\$/year	7	7
Capital cost charge	M\$/year	44	46
Total production cost	M\$/year	176	176
	\$/ton of bio-crude	377	378
	\$/GJ of bio-crude	12.2	12.2
Break-even crude price	\$/bbl	54	54

Chapter 8

Liquefaction of lignocellulose in FCC feed: A process concept study

1. Materials

Elemental compositions of the refinery streams are given in Table S 1. Apparent molecular weight distributions of the refinery streams are provided in Figure S 1.

Table S 1: Elemental compositions (w%) of refinery streams.

	C	H	N	S/O*
LCO	86.25	10.27	0.58	2.90
VGO	86.16	10.08	0.78	2.97
Hydrowax	83.56	11.50	0.52	4.11
Basra crude	82.17	8.95	0.86	7.88

*by difference and it is likely to be Sulfur (S)

Figure S 1: Apparent molecular weight distributions of the refinery streams as determined by gel-permeable chromatography (GPC) technique.

2. Solvent screening and process parameter study

The product yields obtained with different water concentrations (0-30 w%) in LCO and VGO are shown in Figure S 2a. The presence of 10 w% water was found beneficial in the case of VGO but unnecessary in case of LCO. Moreover, when the water concentration was increased to 30 w%, LCO showed a better liquid yield. However, it also resulted in a very high reactor pressure of ~140 bar compared to ~50 bar obtained in a water free operation.

The product yields obtained without water at different reaction times (10-15 min) and different wood loadings (30-40 w%) in LCO are shown in Figure S 2b.

Figure S 2: Product yields of the liquefaction of pine wood in (a) VGO and LCO with different water concentrations. T : 320°C, Feed (Solvent:Wood:Water) = 80- X :20: X w%, (b) LCO only without water at two different reaction times and two different feed compositions. T : 320°C.

Figure S 3 shows the product yields obtained with different wood loadings in LCO as solvent, and at two reaction times (15 and 30 min).

Figure S 3: Product yields of the liquefaction of wood in LCO with different wood loadings and reaction times. T : 320°C, Feed (Sol:Wood:Water) = (90- X): X :10 w%.

3. Liquefaction in VGO: Organics and water yields calculation

Mass and elemental (C and H) balances were used to calculate the amount of the bio-crude-rich phase and the water produced in the reaction. The feed and the product constituents are shown in reaction scheme r-1.

Here there are three unknowns those are mass of the bio-crude-rich phase, water and the VGO-rich phase which can be obtained through solving three balance equations i.e. total mass balance, carbon balance and hydrogen balance, and shown in Table S 2. Water content in the bio-crude-rich phase and in the VGO-rich phase were measured to be 8 w% and 0.8 w% respectively. From that the total water produced in the reaction can be calculated, and hence the total organic yield.

$$\Delta H_R = \sum HHV_{\text{Products}} - \sum HHV_{\text{Wood}} \quad (\text{S.1})$$

Based on the product yields, and HHV of the wood and of the various products, the heat of liquefaction reaction was calculated (equation S.1) to be a moderately exothermic with -0.46 MJ/kg of wood. This corresponds to an adiabatic temperature rise of the total reactor intake by $\sim 50^{\circ}\text{C}$.

Table S 2: Elemental analysis of different components, and products distribution calculated by balance. Bold numbers are calculated by balance.

	Wood	VGO	Water	Bio-crude-rich phase ^a	Char	Gas	Water	VGO-rich phase ^b
EA (w%)								
C	46.58	86.16	0.00	69.18	74.85	31.46	0.00	83.53
H	6.34	10.08	11.11	7.50	4.59	1.25	11.11	10.12
O ^c	46.98	3.75	88.89	23.32	20.56	67.29	88.89	6.35
Mass (g)	4.02	14.01	2.05	2.62	0.85	0.48	2.55	13.58
HHV (MJ/kg)	19.25	44.60	0	30.72	29.71	1.61	0	43.73
Heat of reaction	-0.46 MJ/kg of wood							

^awet (8 w%), ^bwet (0.8 w%), ^cby difference

4. Process simulation

Process flow diagram of the process without filtration of the solids is shown in Figure S 4.

Figure S 4: Process flow diagram of liquefaction of wood in VGO without filtration of the solids. Water can be recycled to the liquefaction reactor in case dry wood is used.

Ideal material balance was used for the process streams of the two process concepts that can be obtained from the material balance around the reactor (Table S 3). Material balance around the liquefaction reactor is shown in Table S 3, which is same for the two process concepts. Energy duties (in GJ/h) of the process equipment are provided in Table S 4.

Table S 3: Material balance around the liquefaction reactor. T : 370°C, time: 30 min.

	Liquefaction reactor (ton/h)					
	Wood	VGO	Water	Bio-crude	Off gases	Char
Rct-Feed	100	350	50	0	0	0
Rct-effluent	0	350	70	47	12	21

Table S 4: Heat duties of the heat transfer equipment of the process. Minimum approach temperature was set at 10°C in the heat exchanger.

	With solids removal		Without solids removal		Remarks
	Heat transfer (GJ/h)	% HHV of wood	Heat transfer (GJ/h)	% HHV of wood	
Feed pump	7.2	0.37	7.2	0.37	Electrical
Feed HE	430	N/A	462	N/A	Heat exchanger
Feed heater	47.1	2.45	15.1	0.80	Heating
Solid drying	28.1	1.46	N/A	N/A	Heating
Condenser	30.6	N/A	N/A	N/A	Cooling

Chapter 9

Liquefaction of lignocellulose in Light cycle oil: A process concept study

1. Experimental

The schematic diagram of the experimental procedure of the refill experiments is shown in Figure S 1.

Figure S 1: Experimental procedure of refill experiments.

2. Product yields and energy distribution

The product yields of the liquefaction in LCO are shown in Figure S 1 for two different reaction times and for two different feed compositions, in absence of external water.

Figure S 1: Product yields of the liquefaction of wood in LCO without water at two different reaction times and two different feed compositions. T : 320°C. Autoclave: 45 mL.

Product yields (w%) obtained in the refill runs (in the 45 mL autoclave) are shown in Figure S 2 which shows similar product yields namely liquid ~68 w%, solid ~26 w% and gas ~6 w% in all the refill runs.

Break-down of the energy present in the wood (based on HHV):

$$\begin{aligned} \text{Energy in char (\%)} &= (\text{mass of char} \times \text{HHV of char}) / (\text{mass of wood} \times \text{HHV of wood}) \times 100 \\ &= 35 \% \text{ HHV} \end{aligned}$$

$$\begin{aligned} \text{Energy in gas (\%)} &= (\text{mass of gas} \times \text{HHV of gas}) / (\text{mass of wood} \times \text{HHV of wood}) \times 100 \\ &= 1 \% \text{ HHV} \end{aligned}$$

Heat of reaction was assumed to be the same as found in the previous chapter with VGO, which was 2.5 % (exothermic) of HHV of wood.

$$\text{Energy in bio-crude} = 100 - (35 + 1 + 2.5) = 61.5 \% \text{ HHV}$$

Figure S 2: Product yields obtained in the refill runs using the separated LCO-rich phase in the 45 mL autoclave, τ : 15 min, Feed (w%); Solvent:Wood = 80:20, T : 320°C.

3. GPC figures

Apparent molecular weight distributions of the LCO-rich phase and the bio-crude-rich phase obtained in the refill runs are shown in Figure S 3. It is likely that the peak at around 60 Da in the GPC of the bio-crude-rich phase is due to the presence of LCO while a slight growing of heavy tail ($M_{w,GPC} > 150$ Da) in the GPC of the LCO-rich phase would likely due to the presence of the bio-crude.

Figure S 3: Apparent molecular weight distributions of (a) LCO/LCO-rich phase and (b) bio-crude-rich phase obtained after the refill experiments. Autoclave: 45 mL, τ : 15 min, Feed (w%); Solvent:Wood = 80:20, T : 320°C. Blank run is without wood.

4. Process simulation

Process flow diagram of the process concept with filtration of the solids is shown in Figure S 4.

Figure S 4: Process flow diagram of liquefaction of wood in LCO with filtration of solids.

Ideal material balance was used for the process streams of the two process concepts that can be obtained from the material balance around the reactor (Table S 1). Material balance around the liquefaction reactor is shown in Table S 1 which is same for the two process concepts. Energy duties (in GJ/h) of the process equipment are provided in Table S 2.

Table S 1: Material balance around the liquefaction reactor. T : 320°C, τ : 15 min.

	Liquefaction reactor (ton/h)					
	Wood	LCO	Water	Bio-crude	Off gases	Char
Rct-Feed	100	350	0	0	0	0
Rct-effluent	0	350	20	48	6	26

Table S 2: Heat duty of heat transfer equipment of the process. Minimum approach temperature was set at 10°C in a heat exchanger.

	Heat transfer (MW)	% HHV of wood	Remarks	Temp. Change (Hot side/Cold side), °C
Feed pump	1.8*	0.34	Electrical	
Feed HE	86.8	N/A	Heat exchanger	(320-78)/(64-310)
Feed heater	4.2	0.80	Heating	310-320
Vacuum	9.1	1.7	Heating	
Vac. drying	7.2	N/A	Cooling	

**Energy consumption*

References

- (1) Nielsen, R. P.; Olofsson, G.; Søgaaard, E. G. CatLiq – High pressure and temperature catalytic conversion of biomass: The CatLiq technology in relation to other thermochemical conversion technologies. *Biomass and Bioenergy* **2012**, 39 (0), 399-402.
- (2) <http://www.altacaenerji.com/en/TeknolojininGeriPlani.html> [accessed 07 . 07 . 2015]. (accessed 7th July).
- (3) http://altaca.com/index_pages_22.html [accessed on 07 . 07 . 2015] (accessed 7th July).
- (4) <http://www.biofuelsdigest.com/bdigest/2015/06/04/4-minutes-with-taner-onoglu-vice-president-altaca-energy/> [accessed 08 . 07 . 2015].
- (5) Molton, P. M.; Fassbender, A. G.; Brown, M. D. *STORS: The sludge-to-oil reactor system*. US Environmental Protection Agency, Water Engineering Research Laboratory: 1986.
- (6) Itoh, S.; Suzuki, A.; Nakamura, T.; Yokoyama, S.-y. Production of heavy oil from sewage sludge by direct thermochemical liquefaction. *Desalination* **1994**, 98 (1–3), 127-133.
- (7) <http://www.water-technology.net/projects/stors/> [accessed 07 . 07 . 2015]. (accessed 7th July).
- (8) http://www.swrcb.ca.gov/lahtontan/board_info/agenda/2010/mar/4_attachment_8.pdf [accessed 07 . 07 . 2015].
- (9) Baskis, P. T. Thermal depolymerizing reforming process and apparatus. Patent US 5269947 A. 1993.
- (10) http://peswiki.com/index.php/Directory:Changing_World_Technology_-_Thermal_Depolymerization_Process [accessed 08 . 07 . 2015].
- (11) Adams, T.; Appel, B. In *Converting turkey offal into bio-derived hydrocarbon oil with the {CWT} thermal process*, Power-Gen Renewable Energy Conference, 2004.
- (12) Cornerstone Technology: Thermal Conversion Process (TCP), Changing World Technologies, Inc. & Affiliate Companies
<http://www.calrecycle.ca.gov/SWFacilities/TechServices/EmergingTech/TCP.pdf>.
- (13) <http://www.energytrendsinsider.com/2009/03/13/update-on-cwt-ipo/> [accessed 07 . 07 . 2015]. (accessed 7th July).
- (14) Bouvier, J. M.; Gelus, M.; Maugendre, S. Wood liquefaction—An overview. *Applied Energy* **1988**, 30 (2), 85-98.
- (15) Chornet, E.; Overend, R. Biomass Liquefaction: An Overview. In *Fundamentals of Thermochemical Biomass Conversion*, Overend, R. P.; Milne, T. A.; Mudge, L. K., Eds. Springer Netherlands: 1985; pp 967-1002.
- (16) Behrendt, F.; Neubauer, Y.; Oevermann, M.; Wilmes, B.; Zobel, N. Direct Liquefaction of Biomass. *Chem. Eng. Technol.* **2008**, 31 (5), 667-677.
- (17) Toor, S. S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* **2011**, 36 (5), 2328-2342.

- (18) Goudriaan, F.; Peferoen, D. G. R. Liquid fuels from biomass via a hydrothermal process. *Chemical Engineering Science* **1990**, *45* (8), 2729-2734.
- (19) Naber, J. E.; Goudriaan, F. Biofuel BV, Successfully using Biomass to Harness Renewable Energy in an Efficient and Cost-effective Way, 2000 in <http://www.cpi.umist.ac.uk/eminent/Confidential/meeting/RigaMeeting/Riga%20Workshop/PresenatieHTUBiofuel.ppt>.
- (20) Westerhof, R.; Kuipers, N.; Kersten, S.; van Swaaij, W. Controlling the Water Content of Biomass Fast Pyrolysis Oil. *Industrial & Engineering Chemistry Research* **2007**, *46* (26), 9238-9247.
- (21) de Miguel Mercader, F.; Groeneveld, M.; Kersten, S.; Geantet, C.; Toussaint, G.; Way, N.; Schaverien, C.; Hogendoorn, K. Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. *Energy Environ. Sci.* **2011**, *4* (3), 985-997.
- (22) van Rossum, G.; Zhao, W.; Castellvi Barnes, M.; Lange, J.-P.; Kersten, S. Liquefaction of Lignocellulosic Biomass: Solvent, Process Parameter, and Recycle Oil Screening. *ChemSusChem* **2014**, *7* (1), 253-259.
- (23) Oasmaa, A.; Elliott, D.; Korhonen, J. Acidity of Biomass Fast Pyrolysis Bio-oils. *Energy Fuels* **2010**, *24* (12), 6548-6554.
- (24) Chen, N.; Degnan, T.; Koenig, L. Liquid fuel from carbohydrates. *Chemtech* **1986**, *16* (8), 506-511.
- (25) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook, Second Edition*. CRC Press: 2007.
- (26) VCCLab. <http://www.vcclab.org/lab/alogps/>.
- (27) J., S. Octanol-water Partition Coefficients for Simple Organic Compounds. *J. Phys. Chem. Ref. Data* **1989**, *18*.
- (28) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*.
- (29) Moffatt, J. M.; Overend, R. P. Direct liquefaction of wood through solvolysis and catalytic hydrodeoxygenation: an engineering assessment. *Biomass* **1985**, *7* (2), 99-123.
- (30) Dai, J.; Cui, H.; Grace, J. R. Biomass feeding for thermochemical reactors. *Progress in Energy and Combustion Science* **2012**, *38* (5), 716-736.
- (31) Wilén, C.; Rautalin, A. Handling and feeding of biomass to pressurized reactors: Safety engineering. *Bioresource Technology* **1993**, *46* (1-2), 77-85.
- (32) Cummer, K. R.; Brown, R. C. Ancillary equipment for biomass gasification. *Biomass and Bioenergy* **2002**, *23* (2), 113-128.
- (33) Loh, H. P.; Lyons, J.; White, C. W. Process equipment cost estimation. *National Energy Technology Center, Report No. DOE/NETL-2002/1169* **2002**.
- (34) Rautalin, A.; Wilén, C.; Valtion teknillinen tutkimuskeskus. Polttoainetekniikan, I.; International Energy, A.; Oy, A. A.; Imatran Voima, O. *Feeding Biomass Into Pressure and Related Safety*

Engineering. Technical Research Centre of Finland, Laboratory of Fuel and Process Technology: 1992.

(35) White, D. H.; Wolf, D.; Zhao, Y. Biomass liquefaction utilizing extruder-feeder reactor system. *Amer. Chem. Soc., Div. Fuel Chem. Prprts.* **1987**, 32 (2), 106.

(36) Brown, R. C.; Stevens, C. *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*. Wiley: 2011.

(37) Douglas, J. M. *Conceptual design of chemical processes*. McGraw-Hill: 1988.

(38) Lange, J.-P. Fuels and Chemicals Manufacturing; Guidelines for Understanding and Minimizing the Production Costs. *CATTECH* **2001**, 5 (2), 82-95.