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Liquefaction of Lignocellulose in Fractionated Light Bio-Oil: Proof of Concept and Techno-Economic Assessment

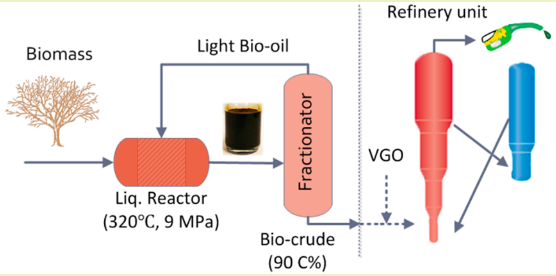
Shushil Kumar,[†] Jean-Paul Lange,*[,†,‡] Guus V. Rossum,[†,‡] and Sascha R. A. Kersten[†]

[†]Sustainable Process Technology, Faculty of Science and Technology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands

[‡]Shell Technology Centre Amsterdam, Shell Global Solutions International B.V., Grasweg 31, 1031 HW Amsterdam, The Netherlands

Supporting Information

ABSTRACT: The direct thermal liquefaction of lignocellulose can provide a biocrude that could be used as a precursor for biofuels. However, earlier attempts to use the whole reactor effluent as a liquefaction medium, by recycling it to the liquefaction reactor, were hampered by the buildup of heavy products. This paper reports on the integration of the liquefaction reaction and the fractionation of the reactor effluent to recover and recycle the light oil fraction of it to be used as a liquefaction solvent. The fractionation is based on solvent extraction and temperature-swing regeneration. Here, we demonstrate steady-state liquefaction of pine wood with high and constant liquid yields (90 C %) and constant liquid qualities over several recycles. The liquefaction was done at a temperature of 320 °C and at a pressure of 7−10 MPa. Process simulation confirms a significant savings in energy demand by incorporating the extraction in the process, compared to an alternative liquefaction/distillation scheme. A techno-economic assessment further estimates that a biocrude could be produced at an energy-equivalent crude oil price of 54 \$/barrel at a wood cost of 85 \$/dry ton.



KEYWORDS: *Liquefaction, Lignocellulose, Extraction, Fractionation, Biocrude, Bio-oil, Techno-economic evaluation, Biomass*

INTRODUCTION

The direct thermal liquefaction of lignocellulosic biomass is a variation of the pyrolysis process for the production of biocrude, which operates under liquid phase conditions and at a moderate temperature of around 250−350 °C.[1−3] Such a liquefaction process can be integrated within an existing manufacturing complex such as an oil refinery, where the produced biocrude is further converted into advanced biofuels or used as a direct fuel. However, it can also be designed as a remote/distributed small scale process located where biomass is available. The produced biocrude can then be transported to a central location for further processing or for its direct use. As an example the biocrude may be coprocessed with a fossil feed to obtain a product that can be blended in the refinery process chain, taking advantage of existing distribution networks. A remote liquefaction process would reduce the transportation cost of biomass because of significant energy densification achieved upon converting biomass at 1.5−7.0 GJ/m^3[4,5] to biocrude (from liquefaction) at 30−40 GJ/m^3.[2] Earlier processes on the direct liquefaction, namely those developed by the Pittsburgh Energy Research Center (PERC),[3,6] and the Lawrence Berkeley Laboratory (LBL)[7] as well as the Hydrothermal Upgrading (HTU)[8,9] process could not reach the commercial stage mainly due to economic reasons associated with high pressure conditions, low oil yield, poor oil quality etc.[2,3,10,11]

Our group[12] also studied the direct liquefaction of lignocellulosic biomass. First we used (like PERC) the whole liquid (reactor) effluent as a liquefaction solvent. The recycling of the whole liquid effluent initially delivered a high oil yield but readily lost its effectiveness as the liquid medium became very viscous due to buildup of heavy product (M_W > 1000 Da) that slowly displaced the light start-up solvent.[12,13] Further optimization of process parameters had limited success in reducing the formation of the heavy product.[14] The use of basic additives helped in reducing the formation of the heavy product but eventually failed upon recycling as it catalyzed the decomposition and condensation of the liquid effluent.[15] This led us to explore fractionation of the liquid effluent into a light and a heavy fraction, and to recycle the former as a liquefaction solvent. Fractionation of the liquid effluent was successfully demonstrated using a new approach that is based on extraction of the lighter components at elevated temperature and recovery of the extraction solvent through spontaneous liquid/liquid phase separation upon cooling.[16] Temperature swing is usually less energy demanding than the conventional extraction solvent recovery by stripping or distillation widely used in the industry.

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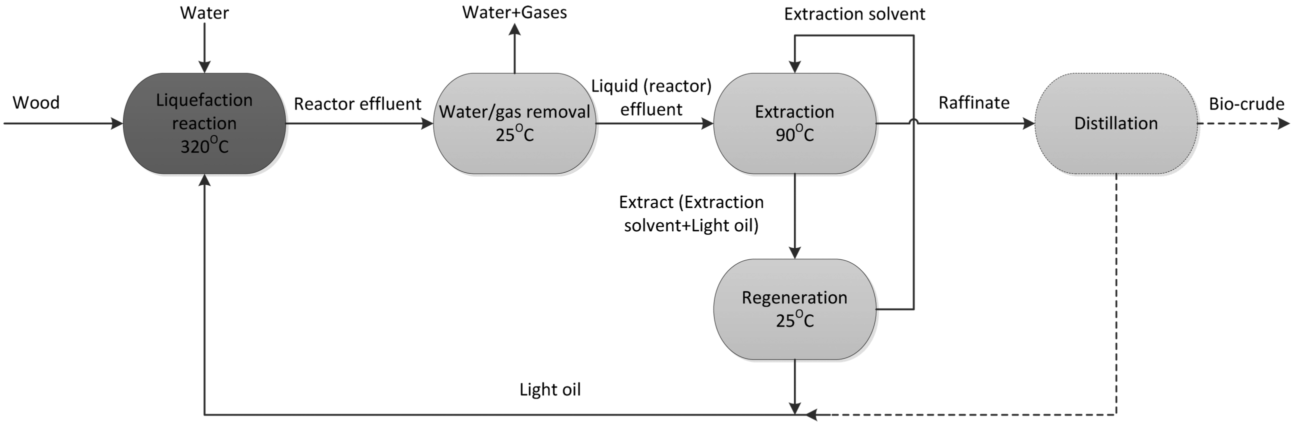

Figure 1. Direct liquefaction process concept with fractionation of the liquid effluent. Solid lines show the route experimentally explored in this work. Dotted lines show the additional distillation unit that may be required in an actual process to recover the balance amount of the light oil. Experimental temperature used in a process is also shown.

The objective of the present work is to integrate the fractionation of the liquid effluent with the liquefaction reaction by recycling the light fraction of the effluent to the reactor to produce the product referred to as biocrude. Figure 1 shows the conceptual block diagram in which the named streams are also indicated. The process concept is explored experimentally through a series of liquefaction runs with intermittent extraction, and recycle of the light fraction (light oil) as a liquefaction medium.

The liquefaction is done at a temperature of 320 °C, which was found optimum in our previous study,[14] and at an autogenous pressure of 7−10 MPa. Water is used here as it accelerates the liquefaction reaction,[14] which will result in a smaller reactor. However, water will also increase the reactor pressure. Additional water or recycling of water will not be required when a wet biomass is used. The reactor pressure is significantly lower than the ~20 MPa pressure in the earlier processes, such the PERC, LBL[2,3,10] and the HTL processes.[9,17] The moderate pressure applied here results from the use of a relatively heavy liquefaction solvent and the omission of reactive gases. A process simulation is carried out to determine the preliminary energy demand of the process. Finally, a techno-economic assessment of the process is carried out to assess the economic potential of the liquefaction process.

■ EXPERIMENTAL SECTION

Materials. Pine wood was obtained from Rettenmaier & Sohne GmbH (Germany). It was crushed to a particle size of <0.5 mm and then dried at 105 °C for 24 h in an oven. The composition of the pine wood is provided in the Supporting Information. All other chemicals were obtained from Sigma-Aldrich with a purity of >98%.

Product Definition and Calculation. Gas, liquid and solid yields were calculated as carbon-fraction of the wood intake (eqs 1−3; excluding liquefaction solvent) rather than the more common weight fraction to avoid counting the oxygen content or water as valuable product.

The gas yield was calculated using the composition analyzed by the off-line GC, available gas volume and, end pressure and temperature after cooling, using the ideal gas law and defining the available gas volume as being the total volume of the reactor minus the volume of the liquid product. The solid yield was determined based on the weight fraction of the solid residue and its carbon content. The liquid yield was obtained by difference. This assumes that the liquefaction solvent does not produce solid and gases, which was verified in our earlier work.[14]

$$\text{yield}_{\text{solid}}\ (\text{C }\%) = \frac{M_{\text{acetone insoluble}}}{M_{\text{wood intake (dry)}}} \times 100 \tag{1}$$

$$\text{yield}_{\text{gas}}\ (\text{C }\%) = \frac{M_{\text{gas formed}}}{M_{\text{wood intake (dry)}}} \times 100 \tag{2}$$

$$\text{yield}_{\text{liquid}}\ (\text{C }\%) = 100 - \text{yield}_{\text{solid}}\ (\text{C }\%) - \text{yield}_{\text{gas}}\ (\text{C }\%) \tag{3}$$

here, M stands for total mass of the carbon in the component.

Furthermore, the liquid was divided into organic and water fractions, and their yields were estimated by solving mass and carbon balances over the reactor using measured masses and carbon contents of reactor feed and products (see the Supporting Information for details).

Any liquid organic stream (liquid effluent, extract or raffinate) was divided into two fractions, based on apparent molecular weight as determined by GPC, namely "Lights" with $M_{\text{W,GPC}} < 1000$ Da and "Heavies or Vacuum residue" with $M_{\text{W,GPC}} > 1000$ Da.

"Liquid (reactor) effluent" was defined as the outlet stream of the liquefaction reactor after removing water and gases (and a very small amount of solid as well) as demonstrated in Figure 1.

"Light oil" was defined as the light fraction of the liquid effluent that is extracted and recycled as the liquefaction solvent after recovery of the extraction solvent.

"Biocrude" was defined as the liquefaction product that is after recovering and recycling the liquefaction solvent (Figure 1). Ideally, the biocrude is a once-through reactor product.

Vacuum Residue (VR) Fraction. Fraction of a liquid that was found in the vacuum residue/heavies based on eq 4. It was calculated using the GPC curve of the liquid, and assumed a comparable response factor for the lights and the heavies.

$$\text{vacuum residue (VR) fraction} = \frac{\text{area corresponds to } M_{\text{W,GPC}} > 1000 \text{ Da}}{\text{total GPC area}} \tag{4}$$

Extracted Percentage. Percentage of the feed (liquid effluent) that was extracted by the extraction solvent and found in the extract, as defined by eq 5.

$$\text{extracted percentage} = \left(1 - \frac{\text{mass of raffinate}}{\text{mass of liquid effluent}}\right) \times 100 \tag{5}$$

Cumulative Wood Percentage. The cumulative wood percentage is introduced as an 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 toward 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 makeup solvent used in that specific run eq 6. Interestingly, the cumulative wood percentage also represents roughly the concentration of wood-derived components in the recycle solvent when the whole liquid effluent is recycled as the reaction solvent.

$$\text{cum. wood in run ``}i\text{'' (wt \%)} = \frac{\text{wood (g)} + \text{recycle solvent (g)} \times \text{cum. wood in run ``}i-1\text{'' (wt \%)}/100}{\text{wood (g)} + \text{recycle solvent (g)} + \text{make-up solvent (g)}} \times 100 \tag{6}$$

For the first run, the recycle solvent is zero.

Experimental Setup and Procedure. The concept of extraction of the light oil and its recycle was investigated by performing several consecutive liquefaction experiments with intermittent extraction and recycle of the light oil. First a liquefaction experiment was carried out at 320 °C for 30 min, in a 45 mL batch autoclave using a feed of guaiacol:wood:water of 55:30:15 in a weight ratio. In this work, guaiacol was used as a start-up liquefaction solvent that was replaced by the fractionated light oil that builds up upon recycling. The experimental setup and the procedure for the liquefaction of wood is described elsewhere in detail.[14] Hexadecane was selected as an extraction solvent.[16] The resulting liquid effluent from the liquefaction experiment was subjected to a 2-stage extraction with a 5-fold volume of hexadecane as demonstrated in Figure 2. The extraction was carried out in a laboratory glass beaker that was heated using a temperature controlled electrical heating plate and stirred using a magnetic stirrer. The mixture was stirred for half an hour at 90 °C, and then phases were allowed to settle down for a phase split at 90 °C. The resulting two phases, namely extract and raffinate, were separated using a syringe. The extract was cooled down to room temperature, which resulted in an another phase split of the extracted light oil and a nearly pure hexadecane phase (the regenerated extraction solvent). The raffinate remained a single phase even when cooled down to room temperature. In order to extract more light oil from the raffinate, the raffinate was subjected to a second stage extraction using the extraction solvent regenerated in the first stage, following the same procedure as used in the first stage. The light oils recovered in the first and second stages were mixed together and used as a liquefaction solvent for a second liquefaction run and a second extraction step. This procedure was followed for five liquefaction runs and subsequent extraction steps. In all the liquefaction runs, the feed composition was kept the same, i.e., solvent(liquefaction):wood:water of 55:30:15 in a weight ratio. Some fresh guaiacol was added to the second liquefaction run only in order to makeup for the loss incurred to saturate the extraction solvent with guaiacol in the very first extraction step.

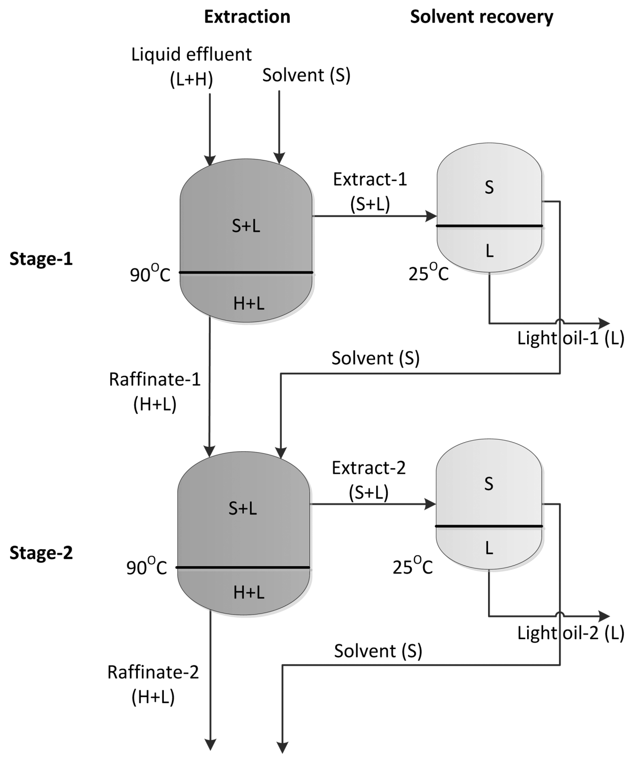

Figure 2. Experimental procedure of 2-stage extraction with intermediate solvent (extraction) regeneration. Lights, L; heavies, H; solvent, S. Major components present in a phase or in a stream are also shown.

Analyses. Gas samples were analyzed with an off-line gas chromatography instrument (Varian Micro GC CP-4900). The liquid samples were analyzed with gel permeation chromatography (GPC; Agilent 1200 series, with RI and UV (wavelength: 254 nm) detectors), using 3 GPC PLgel 3 μm MIXED-E columns connected in series. More details about the equipment can be found elsewhere.[15] The elemental composition was determined using an elemental analyzer (Interscience Flash 2000). The chemical nature (bond types) was investigated by means of a Fourier transform infrared spectrophotometry instrument (FTIR, Bruker Tensor 27). The water content of the liquid samples 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. Microcarbon tests (MCRT) were performed following the ASTM D4530 standard.

RESULTS

Product Yields upon Recycling. Having shown the principle of recovering the light oil from the liquefaction liquid effluent in our earlier work,[16] we needed to integrate it in a liquefaction scheme to selectively recover and recycle the light oil. The recycle of the light oil was meant to minimize the buildup of the heavies and, thereby, to avoid the increase in the viscosity of the liquefaction medium seen previously.[12,13]

Hexadecane was used here as an extraction solvent. As the number of liquefaction−separation cycles increased, the product yields were found stable (Figure 3). A very high liquid yield of ∼90 C % and a low gas yield of ∼10 C % were obtained in all the refill experiments with intermediate fractionation. The solid yield was negligible. The five successive runs achieved a cumulative wood loading of 85 wt %, whereas infinite recycle

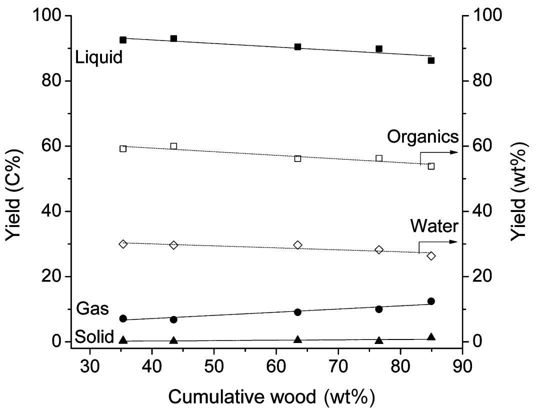

Figure 3. Product yields obtained in the liquefaction runs with intermediate fractionation. Liquid is further divided into organics and water (open symbols). Lines are linear fitting of the data. Liquefaction feed (wt %); solvent:wood:water = 55:30:15, T = 320 °C, τ = 30 min, extraction T = 90 °C, recovery T = 25 °C, extraction solvent = hexadecane.

would correspond to the cumulative wood loading of 100 wt %, as defined earlier in eq 6. These results show that a stable liquefaction process, in terms of product yields, can be developed by implementing an intermediate fractionation step. Product yields in wt % are provided in the Supporting Information.

After the reaction, two liquid phases were obtained, namely an aqueous phase at the top and an organic phase at the bottom. The water content of the organic phase was ~6 wt % whereas it was ~90 wt % for the aqueous phase. Only the organic phase was used for the extraction and for the analyses. After the extraction, the extracted light oil contained ~5 wt % water whereas the extraction solvent had a negligible amount of water. The raffinate obtained after the second-stage extraction was solid at room temperature. It started to melt at ~70 °C and became fluid at ~110 °C.

The small size of the reactor and the complex product collection process made it difficult to measure accurately the amount of organics and water fractions produced during the liquefaction reaction. Therefore, yields of the organics and water were estimated based on mass and carbon balances of the reaction products, and found stable as well (Figure 3). The organic yield was estimated to be ~56% based on weight, ~90% based on carbon and ~93% based on energy content (see the Supporting Information for calculation). The yield of water (produced) was estimated to be ~30 wt %.

Product Quality upon Recycling. The VR fraction in the liquid effluent increased only moderately upon increasing the number of liquefaction–separation cycles (Figure 4a). This increase was much less than the nearly exponential increase that can be derived from the data reported upon recycle of the full liquid effluent without intermittent fractionation[12] (Figure 4a). Upon extrapolation to 100% cumulative wood, that is to steady state recycle operation, the VR fraction stabilizes at around 0.25 in the case of intermittent fractionation whereas it rises about exponentially to 0.90 without fractionation. In the calculation of the VR fraction, the GPC response factor of the lights and the heavies were assumed to be equal. However, the response factor of the raffinate (rich in heavies) was found to be ~40% larger than the response factor of the extracted light oil (rich in lights), thereby the actual VR fraction would be even lower. It should be noted here that the VR fraction is defined as a fraction of the liquid effluent which also includes the liquefaction solvent. A similar stabilization of the VR fraction is also found when the VR fraction is defined on liquefaction solvent-free liquid effluent, as defined in our earlier papers[14,15] (see the Supporting Information).

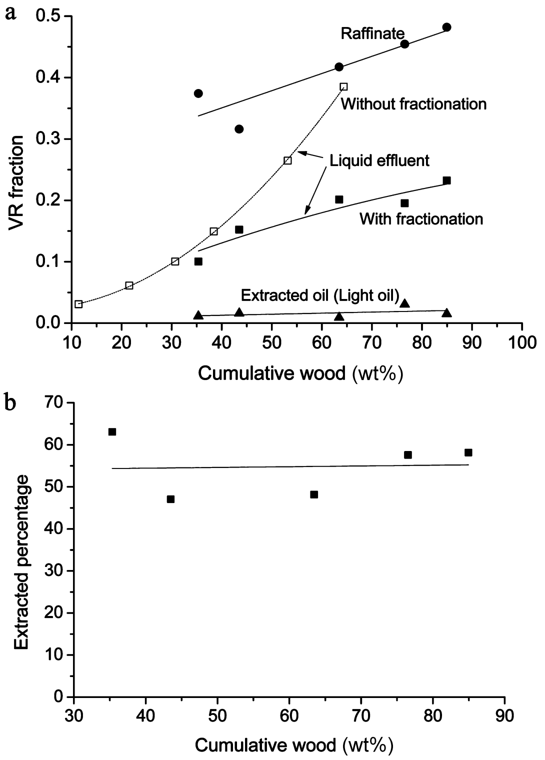

Figure 4. (a) Buildup of the VR fraction in the liquid effluent upon cumulative recycle with and without intermediate fractionation, and buildup of the VR fraction in the other streams obtained upon extraction and recycling of the light oil; (b) extracted percentage in all the five extraction runs (only in the first stage). Liquefaction T = 320 °C, τ = 30 min, extraction T = 90 °C, recovery T = 25 °C.

The increase in the VR fraction in the liquid effluent also resulted in a similar increase in the VR fraction in the raffinate (Figure 4a), which reaches ~0.5 at steady state (100 wt % wood loading). Interestingly, no significant buildup of the VR fraction was observed in the extracted light oil (Figure 4a). Stability of the extraction was confirmed by a constant extracted percentage (~55%) upon consecutive recycling (Figure 4b). The extracted percentage was not improved significantly in the second stage extraction (see the Supporting Information) and hence a second stage extraction will not be economical from a process point of view. Alternative to a nonpolar solvent hexadecane, a polar solvent such as water/methanol mixture can be used as an extraction solvent, which showed a cumulative extracted percentage of 90 wt % in four stages in our previous work.[16]

A check on constant product quality was done by characterizing the raffinates for their elemental compositions, heating values, coking tendencies (carbon residue content as determined by the Micro Carbon Residue Test (MCRT)) and chemical functionalities (using FTIR). The results show that the raffinates hardly differ in their elemental compositions, higher heating values (HHV) or carbon residue (MCRT) as shown in Table 1. Steady-state quality of the raffinates in terms of chemical functionalities was also confirmed by inspection of their FTIR spectra, upon successive recycle. This can be illustrated by Figure 5, which shows a fairly constant ratio between characteristic FTIR bands, namely the C═O band (in aldehydes, ketones acids and/or esters, 1698 cm^{-1}), the C—O band (in alcohol and/or ether; 1023 cm^{-1}) and the C═C band (in aromatic skeleton; 1596 cm^{-1}) with respect to the C—H band (in methyl and methylene; 2922 cm^{-1}). When these relative intensities in the raffinates were compared with the relative intensities of these bands in the wood, only the C—O bond was reduced significantly in the raffinates (~7.4 in the wood to ~2.3 in the raffinates), most likely because of the dehydration reaction. The constant ratio between the characteristic FTIR bands cannot be attributed to the presence of guaiacol, since guaiacol has very different relative intensities of the C—O, C═C and C═O bands with respect to the C—H band, namely 14.3, 6.7 and 0.2, respectively.

The raffinates still contain some residual liquefaction solvent due to incomplete recovery of the liquefaction solvent. The fraction of the residual liquefaction solvent in the raffinate was estimated based on GPC area of the peak at around 100 Da (see the Supporting Information for GPC figures), and using a

Table 1. Data on Characterization of the Raffinates[a]

	C (dry wt %)	H (dry wt %)	O (dry wt %)	O/C	H/C_{eff}[b]	water (wt %)	HHV[c] (MJ/kg)	MCRT (dry wt %)	VR frac.	residual solvent (wt %)
raffinate-1 (35)	72.8	6.1	21.1	0.22	0.57	4.1	30.4	39.7	0.37	23
raffinate-2 (43)	72.2	6.3	21.6	0.22	0.59	3.2	30.3	35.5	0.32	38
raffinate-3 (63)	75.0	5.8	19.2	0.19	0.54	6.9	30.9	39.7	0.42	26
raffinate-4 (77)	74.3	6.1	19.5	0.20	0.60	4.3	31.1	45.2	0.45	17
raffinate-5 (85)	74.6	5.8	19.6	0.20	0.54	4.4	30.8	42.5	0.48	18

[a] The number between brackets reports the cumulative wood intake. [b] $(H - 2 \times O)/C$; here H, O and C are the atomic composition. [c] Using Reed's equation.[18]

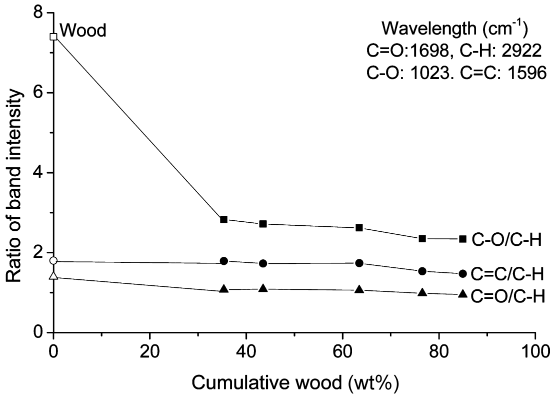

Figure 5. Relative intensities of C═O, C—O and C═C bands with respect to C—H band in FTIR spectra of the raffinates versus cumulative wood. Relative intensities of these bands in the FTIR spectrum of the wood are reported at 0% cumulative wood.

measured GPC response factor of guaiacol. The residual solvent seems to remain constant in the raffinates (except in raffinate-2), as shown in Table 1. The properties of the final product (biocrude) after removal of the residual solvent from the raffinate, will differ slightly from that of the raffinate reported in Table 1, namely a higher MCRT and a higher VR fraction.

The composition of the gas phase (average composition in vol %: 66% CO_2, 27% CO, 5% H_2 and 2% CH_4), water content of the organic phase (~6 wt %) and the aqueous phase (~90 wt %) were found constant with cumulative wood.

■ DISCUSSION

A striking feature of the liquefaction process is the high oil yield that is achieved, namely 90 C % or 93% HHV; this largely exceeds the 50−70 C % (43−66 wt % of organic, excluding ~10 wt % of reaction water) yield that can be estimated from the data reported for fast pyrolysis.[19−25]

The process conditions used here, i.e., temperature of 320 °C and reactor pressure of ~9 MPa, are significantly milder than applied in the earlier processes, e.g., temperature of 330−370 °C and pressure of ~20 MPa in the PERC, LBL and HTL processes.[2,3,9,10,17] The reactor pressure can even be lowered here by not using water in the liquefaction feed and accepting a longer reaction time and a larger reactor. The process does not use any reacting gases or any catalyst unlike the PERC and LBL processes, which used CO/H_2 and Na_2CO_3. Hence, the economics of the present process will likely be better than that of these earlier processes. It is likely that there will be organics lost to the aqueous phase. However, this loss is very low (~5 wt % of wood intake), and may not be economically attractive to recover them as a fuel. Moreover this loss can be further minimized by not using water in the liquefaction feed. The liquefaction process is supposed to build its own light oil and to displace the start-up solvent. At this moment, we can just speculate that a lighter liquefaction solvent is likely better, and that true continuous operation with recycling will require optimization of the molar mass range to be extracted and recycled.

Pyrolysis oil (PO): A liquid obtained in a fast pyrolysis process.
OFWA: Organic fraction obtained after water addition in PO.
Pyrolytic lignin : A precipitate obtained after dropwise adding PO over ice-cooled water while stirring it.
HDO oil : Hydrotreated PO.

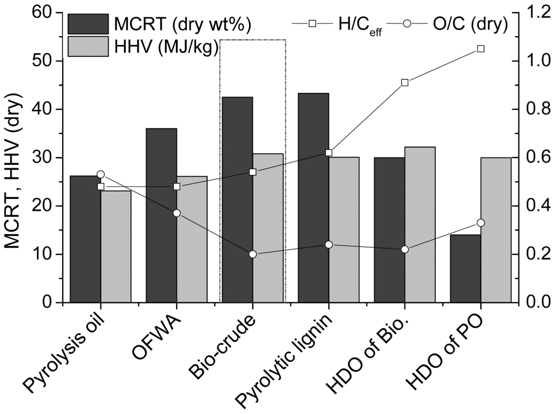

Figure 6. Properties of the biocrude produced in the liquefaction process compared to pyrolysis oil and its derivatives. Data of the raffinate-5 is used as for the biocrude. Data are obtained from these articles: for PO,[26] OFWA,[26] pyrolytic lignin in-house also similar as reported by Marker et al.,[29] HDO of PO at 230 °C.[28] Data for HDO of biocrude (Bio.) at 210 °C (Ru/C 5 wt %) is from an in-house experiment with a similar liquefaction oil.

Furthermore, in an attempt to evaluate the quality of the resulting liquefaction biocrude and to compare it with other oils, namely pyrolysis oil and its derivatives, we have compiled a number of properties for various oils in Figure 6. The properties of pyrolysis oil is obtained from the data reported by Mercader et.al.[26] The pyrolysis oil was produced by VTT (Finland) in a 20 kg/h process development unit[27] using forest residue as feedstock. By mixing the pyrolysis oil and water in a 2:1 weight ratio, two phases were obtained, namely an organic fraction (OFWA) containing 32 wt % of the organics from the whole pyrolysis oil and an aqueous fraction.[26] The properties of hydrotreated pyrolysis oil is taken from the data reported by de Miguel Mercader et al.[28] Hydrotreatment of the whole pyrolysis

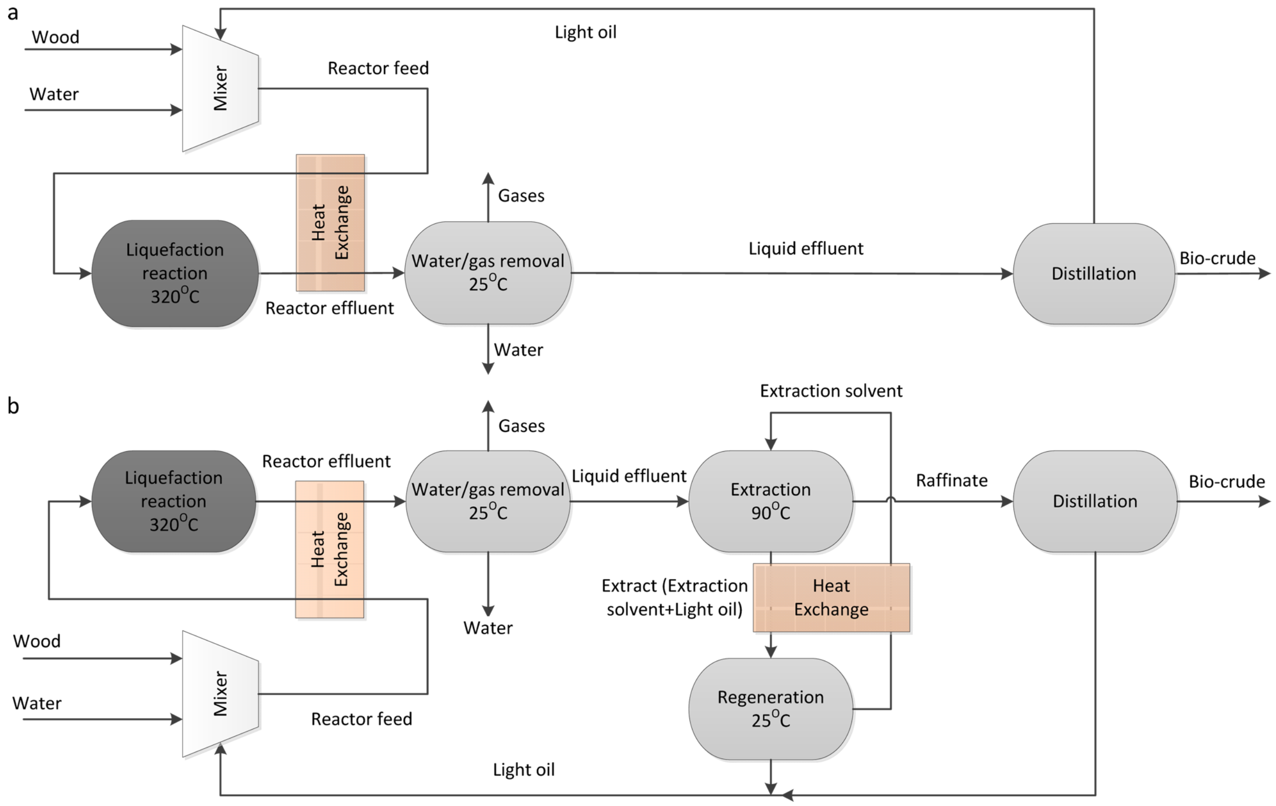

Figure 7. Process block diagram of two process alternatives of direct liquefaction followed by separation of the light oil: (a) distillation to remove the light oil; (b) extraction of the light oil using hexadecane followed by distillation to recover the balance amount of the light oil. Major heat exchanges between streams in a process are shown.

oil (produced by VTT) was carried out in a 5 L autoclave at 230 °C, using H_2 pressure of 29 MPa and using Ru/C (5 wt %) catalyst.[28] Pyrolytic lignin was produced in-house by dropwise adding a pyrolysis oil (10 mL) to 500 mL of cold water (0 °C) while stirring at high speed.[20] Pyrolytic lignin was precipitated as small solid particles at the bottom of the vessel, which were then separated and further washed in excess water for 2 h under slow speed stirring. The pyrolysis oil was obtained in-house in a 1 kg/h process development unit using pine wood as feedstock.[20] Data for HDO of biocrude is taken from an in-house hydrotreatment of a similar liquefaction biocrude at 210 °C using H_2 pressure of 20 MPa and using Ru/C (5 wt %) catalyst in a 560 mL autoclave. Raffinate-5 is used as a liquefaction biocrude that contains around 18 wt % of the liquefaction solvent. Accordingly, the liquefaction biocrude differs significantly from conventional fast pyrolysis oil by showing a favorably higher heating value and lower O/C ratio, and also regrettably a higher MCRT. In fact, the liquefaction biocrude resembles more to the OFWA oil and the pyrolytic lignin in terms of O/C, HHV and MCRT as shown in the Figure 6. However, it does not quite reach the quality of the hydrotreated pyrolysis oil which combines a similarly higher heating value with a lower MCRT.

The liquefaction biocrude could potentially be used as "residual" fuel or it could be further upgraded into transportation fuels by processing it in an oil refinery unit such as an FCC unit. In the absence of FCC test results with the present liquefaction biocrude, we attempted to derive its potential as an FCC feed or a feed blend component by analyzing the literature data. In the past, few attempts have been made to upgrade various bio-oils into transportation fuels by processing them as such or as a blend in a petroleum stream.[26,28−31] The bio-oils consisted mainly of pyrolysis oil and upgraded pyrolysis oils. They showed better operability and product yield in the FCC after hydrotreatment of the bio-oil. These studies attributed the higher cracking yield of the hydrotreated oils to an increase of the H/C_{eff} and/or decrease of the MCRT of the bio-oil, while neglecting the detailed molecular structure of the feed in first instance.[26,28−32] The liquefaction biocrude has H/C_{eff} of 0.54 and MCRT of 42%. Both properties suggest a high coke yield when processing in an FCC unit. Hence, the liquefaction biocrude might require a similar hydrotreatment as pyrolysis oil prior to be processed in an FCC unit. An in-house mild hydrotreatment (Ru/C catalyst, 210 °C, 20 MPa H_2, reaction time of 2 h) of a liquefaction biocrude showed significant reduction in the MCRT and increase in the H/C_{eff} (Figure 6). Further reduction in the MCRT and increase in the H/C_{eff} can be achieved by increasing the severity of the hydrotreatment. MCRT of the biocrude can be decreased (and H/C_{eff} can be increased) also by blending it in a large proportion of fossil feed.[28,33] Such hydrotreatment of the biocrude will obviously require additional equipment, will consume some hydrogen and will result in a loss of carbon, e.g., to gas and coke. However, given the very high liquid yield of the liquefaction process, a small loss of carbon in the hydrotreatment step would still give a higher hydrotreated liquid yield compared to pyrolysis route.

PROCESS SIMULATION AND TECHNO-ECONOMIC ANALYSIS

Process Simulation and Energy Requirements. The integrated liquefaction−fractionation process was modeled and simulated using Aspen Hysys to determine its energy demand and energy transfer requirements. Two modes of fractionation were considered: (1) distillation and (2) single-stage extraction followed by distillation to recover the balance amount of the light oil from the raffinate to close the recycle loop. The process block diagrams of the two process schemes are shown in Figure 7. The second scheme is in fact a hybrid of extraction and distillation, which showed a better balance between Capex (heat transfer duty) and Opex (energy consumption) than a multistage extraction.[16] Note: distillation used here is actually a flash column with reboiler and condenser. Major heat exchanges between streams are shown in Figure 7, whereas the detailed process flow diagram can be found in the Supporting Information.

In the both schemes, the liquefaction reactor is fed with liquefaction solvent, wood and water in 55:30:15 weight ratio. The resulting product yields (based on wood) were taken as 56 wt % organic, 30 wt % water, 14 wt % gas and zero solid, as found experimentally (Figure 3). The organic fraction was assumed to contain the lights and the heavies in 50:50 weight ratio, as found in the final raffinate. The lights were modeled as being guaiacol whereas heavies and wood were modeled as being bisphenol-A.

With the organic yield of 56 wt % from the wood, around 76.6 wt % of the liquid effluent needs to be recovered to close the recycle (reactor feed solvent:wood:water = 55:30:15; liquid effluent (water free) = 55 + 30 × 0.56 = 71.8; percentage of the liquid effluent required to close the recycle = 55/71.8 × 100 = 76.6%).

In the first scheme, the liquid effluent is sent to an atmospheric distillation column (bottom temperature of 320 °C[16]) that recovers 76.6 wt % of the liquid effluent as the light oil for recycling to the liquefaction rector. The remaining 23.4 wt % of the liquid effluent is produced as the biocrude to be used as direct fuel or for further processing to biofuel. In case such high bottom temperature results in coke formation, atmospheric distillation can be replaced by vacuum distillation, which will lower the bottom temperature and hence will avoid coke formation.

In the second scheme, the liquid effluent is first sent to an extraction unit (hexadecane:feed = 4:1 weight ratio, extraction T = 90 °C) to recover 55 wt % of the liquid effluent as the light oil (Figure 4b). The raffinate is processed in a finishing atmospheric distillation column (bottom T = 320 °C) to recover the remaining part of the light oil needed to reach the recovery of 76.6 wt %. The extract is cooled to room temperature to recover the extraction solvent and recycle the light oil back to the liquefaction reactor, as demonstrated in the Experimental Section.

It should be noted here that the fractionation does not need to achieve a deep/higher recovery or a sharp separation of the lights only. It only needs to recover enough (76.6 wt %) of the light oil to close the recycle. The biocrude (product) stream may need further fractionation in the oil refinery to provide specific streams for specific upgrading.

Further processing of the biocrude will likely require high temperature. Therefore, it was chosen to deliver the biocrude at 320 °C; the temperature at which the biocrude is obtained as a distillation bottom product.[16] It assumes that the liquefaction is incorporated in a central facility. However, a remote/distributed small scale liquefaction process with transportation of the biocrude to the central facility can also be an option. This will require delivering the biocrude at low temperature that can be done by installing an additional cooler in the process. Further details of the Aspen Hysys model, procedure and material balance of the two processes can be found in the Supporting Information.

The distillation route has an energy requirement of ~1.7 GJ/t of the wood intake, which is about 9% of the energy equivalent of the wood. For comparison, a pyrolysis reactor can be estimated to consume around 7−10% of the energy equivalent of the wood.[34,35] The overall heat transfer amounts to ~5.9 GJ/t of the wood, of which ~2.3 GJ/t is needed to bring the slurry feed to the reaction temperature.

The extraction route has an energy requirement of ~1.0 GJ/t of the wood intake, which is only 5.5% of the energy equivalent of the wood, ~40% lower than the distillation scheme. The overall heat transfer amounts to ~5.5 GJ/t of the wood, of which ~2.1 GJ/t is needed to bring the feed slurry to the reaction temperature. Detailed simulation methods and material balance of the process streams can be found in the Supporting Information.

Techno-Economic Assessment. Techno-economic assessment of the process concepts was further carried out. The capital cost (inside battery limit cost only) of the two processes could be estimated from the energy transfer duty of each process equipment obtained from process simulation, using the correlation suggested by Lange[36] as given by eq 7. Equation 7 is updated by replacing the original factor of 2.9 with 4.7 to account for cost escalation from year 1993 to 2014 (using chemical engineering plant cost index; CEPCI for year 2014 (July) is 576.9 and for year 1993 is 359.2). The capacity of the plant was arbitrarily set to 100 t/h of dry wood.

$$\begin{aligned}&\text{investment [ISBL, M\$ 2014]}\\&\quad = 4.7 \times (\text{energy transfer [MW]})^{0.55}\end{aligned} \tag{7}$$

The ISBL cost of the two processes were found to be similar, within 10%, around 170 M$ (for year 2014). However, the extraction scheme (with distillation for finishing) has an energy demand around 40% lower than the distillation scheme. The inaccuracy of the capex correlation may not allow reliable discrimination between the two processes based on their capex. A more detailed estimate, e.g., based on equipment list and sizing, would be needed here. There are still ample opportunities to improve the extraction process as reported earlier,[16] which can further reduce its capex and energy requirements.

The total investment costs of the two process schemes were obtained by multiplying the ISBL cost with a factor of 2.26 that takes other costs into account (see the Supporting Information). The energy requirement of the process was met by additional biomass intake (12 wt % in the distillation and 7 wt % in the extraction) assuming an energy conversion of 75% from wood to process stream.

The production cost was estimated and is shown in Table 2 (for detail calculation see SI). The production costs of the biocrude in both process schemes are estimated to be similar at around 378 $/t or 12.2 $/GJ, which corresponds to an energy-equivalent crude-oil price of ~54 $/bbl. The production cost can be divided into three components that are (i) variable operating cost (feedstock, utility) of ~43%, (ii) fixed operating cost (labor, maintenance, overheads, taxes, insurance, lab, royalty) of ~31% and (iii) capital charge of ~26%. The capital charge was estimated with the annuity method employing a 10% interest rate and a service life of 20 years. A similar

Table 2. Process Economics Data of the Two Process Concepts[a]

		distillation	extraction
feed intake	kt/a of dry wood	800	
	t/h of dry wood	100	
product (biocrude)	t/h	56	
biocrude yield[b]	t/t	0.56	
	carbon/carbon	0.90	
	GJ/GJ	0.93	
feed price	$/t of dry wood	85	
	$/GJ	4.6	
energy cost[c]	M$/a	8	5
total investment	M$	375	393
capital charge[d]	M$/a	44	46
total production cost	M$/a	176	176
	$/t of biocrude	377	378
	$/GJ of biocrude	12.2	12.2
break-even crude price	$/bbl	54	54

[a] Operation time = 8300 h/a, a = annum. For detail calculation, see the Supporting Information. [b] Based on wood. [c] Based on additional wood intake and assuming 75% energy efficiency. [d] Determined with the annuity method: 10% rate of return and 20 years of service life corresponds to a capital recovery factor of 0.12.

breakup of the three components was also used by Elliott et al.[37] for the techno-economic assessment of biomass liquefaction processes. The production cost for fast pyrolysis process and for liquefaction process reported by Elliott et al.[38] were 10.5 and 15.5 $/GJ in 1991 currency (wood price: 60 $/dry t) using similar methods.

The investment costs of both liquefaction process concepts are estimated to be similar at 375−395 M$. The investment cost reported by Elliott et al.[38] for a pyrolysis and a liquefaction process, rescaled to 100 t/h of feed and in year 2014, are ∼210 and ∼360 M$, respectively (using power law of 0.7). Other studies also reported that a pyrolysis plant with subsequent upgrading of the bio-oil, rescaled to 100 t/h of feed and in year 2014, had estimated capital costs of around 360 M$[39]−380 M$,[40] and a similar capacity of a bioethanol from corn stover plant had investment cost of 300−500 M$,[41−44] and 500−600 M$[44] for a gasification process. A direct coal liquefaction process with subsequent upgrading to transportation fuels, rescaled to 100 t/h of feed and in year 2014, had estimated capital cost of ∼600 M$.[45]

The higher investment of the liquefaction process, compared to pyrolysis, is due to the oil fractionation and recycle. However, the higher investment is well compensated by the higher biocrude yield (∼90 C %) in the liquefaction process, compared to the oil yield in the pyrolysis process (∼50−70 C %),[19−21,25,46,47] which makes the production cost competitive. The energy yield is also significantly higher in the liquefaction process compared to the pyrolysis.

Building a large scale pyrolysis plant may be hindered by heat transfer limitation[48] and hence multiple parallel units may be required. Liquefaction process possibly will not have such heat transfer limitation as streams subjected to heat exchange are either in liquid phase or in slurry phase. However, feeding a large liquefaction stream of 330 t/h (∼330 m^3/h) against 8−10 MPa may be an issue in the liquefaction process. The reactor pressure is still lower than the pressure in earlier developed process, such as ∼20 MPa in the PERC, LBL and HTL processes.[3,9,17] For the economic evaluation, piston pumps were considered and their installed cost was estimated to be 3 M$,[49,50] which is hardly 2% of the total ISBL cost of the process. A detailed discussion on the selection of the feeding system and their costs can be found in the Supporting Information.

It should be noted here that economic evaluation of the process was done assuming 30 wt % of solid (wood) in the reactor feed mixture that would not be a slurry but a solid soaked with liquid, which may pose problems during pumping. If needed, the wood concentration could be lowered to 15−20 wt % to obtain a slurry. However, lowering the solid content to 20 wt % would increase the energy transfer duty and, thereby, the capital cost by a factor of ∼1.25 (according to eq 7) and would increase the production cost to 13.8 $/GJ or 61 $/barrel of energy-equivalent crude oil price. It also increases the energy consumption to around 13.4% and 8.2% of the energy equivalent of the wood in the distillation and in the extraction concept, respectively.

A likely small loss of organics to the aqueous phase is not considered in the economic assessment. Also the biocrude is slightly acidic (total acid number (TAN) of ∼60[15]) and, hence, might require expensive material for the equipment. This is not captured by the cost−energy correlation used here. These two factors will likely have a negative impact on the economics of the process.

The cost estimation of the liquefaction process here is very preliminary; however, the results show its worth looking further into it.

CONCLUSION

This paper reports the successful integration of the liquefaction and the fractionation to recover and recycle light oil to be used as a liquefaction solvent and to produce a biocrude. The biocrude can be used as a “residual fuel” or as a precursor for advanced biofuels. The fractionation of the liquid effluent is based on extraction and temperature-swing regeneration.

It has been demonstrated, by five consecutive refill runs, that steady state liquefaction of pine wood with constant product yields and constant oil qualities can be achieved. At steady state, the liquefaction process converts pine wood to the biocrude with a very high yield of 90% based on carbon and 93% based on energy content at temperature of 320 °C and pressure of ∼7−10 MPa. The process is accompanied by a moderate gas production (∼10 C %) and a negligible char yield (<1 C %). The oil yield is much higher than reported for pyrolysis.

Characterization of the liquefaction biocrude showed beneficial properties compared to pyrolysis oil, namely a lower oxygen content, a higher H/C_{eff} ratio and a higher energy content. However, it also showed penalties in terms of a higher heavy tail and, consequently, a higher viscosity and a higher coking tendency.

The economic potential of this integrated liquefaction/fractionation process was assessed by process simulation. The evaluation suggests that the biocrude could be produced at 12.2 $/GJ, which corresponds to an energy equivalent crude oil price of 54 $/barrel (at a wood cost of 85 $/t dry). There is still ample scope for improvement in the liquefaction processes, which can make the direct liquefaction process further attractive.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00547.

> Wood characterization (Table S1); Detailed experimental data of extraction experiments (Table S2); GPC graphs of various liquid streams (Figure S1); VR fraction including liquefaction solvent and excluding liquefaction solvent (Figure S2); product yields based on wt % (Figure S3); Gas composition (Figure S4) and FTIR spectra of raffinates (Figure S5); Organic and water yield calculations (equation s1-s3); Process flow sheet of the two process concepts (Figure S6); Material balance (Table S3–S6); Discussion on biomass feeding, techno-economic assessment methods; Detailed data on process economics (Table S7) (PDF).

AUTHOR INFORMATION

Corresponding Author

*J.-P. Lange. E-mail: jean-paul.lange@shell.com.

Notes

The authors declare no competing financial interest.

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ABBREVIATONS

a = annum
bbl = barrel
Da = Dalton
GPC = gel permeable chromatography
h = hour
HHV = higher heating value
$M_{W,GPC}$ = molecular weight defined by GPC
M_W = molecular weight
RID = refractive index detector
T = temperature
τ = reaction time
t = metric ton
VR = vacuum residue

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