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DOI
10.1002/bbb.1999

Publication date
2019

Document Version
Final published version

Published in
Biofuels, Bioproducts and Biorefining

Citation (APA)
Vural Gursel, I., Dijkstra, J. W., Huijgen, W. J. J., & Ramirez, A. (2019). Techno-economic comparative assessment of novel lignin depolymerization routes to bio-based aromatics. *Biofuels, Bioproducts and Biorefining*, *13*(4), 1068-1084. https://doi.org/10.1002/bbb.1999

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Techno-economic comparative assessment of novel lignin depolymerization routes to bio-based aromatics

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Received July 03, 2018; revised February 20, 2019; accepted February 20, 2019
View online April 5, 2019 at Wiley Online Library (wileyonlinelibrary.com);
DOI: 10.1002/bbb.1999; *Biofuels. Bioprod. Bioref*. 13:1068–1084 (2019)

Abstract. This paper presents a techno-economic assessment of three novel routes for the production of bio-based aromatics from lignin. It aims to provide insights into their feasibility and hotspots at an early stage of development to guide further research and development and to facilitate commercialization. The lignin conversion routes are: (non-catalytic) lignin pyrolysis, direct hydrodeoxygenation (HDO), and hydrothermal upgrading (HyThUp). The products generated are mixed oxygenated aromatic monomers (MOAMON), light organics, heavy organics, and char. For the technical assessment, conceptual design followed by process modeling in Aspen Plus was based on experimental yields. The models generated indispensable data on material and energy flows. An economic assessment was then conducted by estimating operating and capital costs. Return on investment (ROI), payback period (PBP), and net present value (NPV) were used as key performance indicators. Downstream processing was especially demanding in the HyThUp process due to the presence of a significant flow rate of water in the system, which significantly increased external utility requirements. Due to complex separations, the HyThUp process showed the highest capital cost (35% more than pyrolysis). Operating costs were the highest for the direct HDO process (34% more than pyrolysis) due to the use of hydrogen. Overall, the direct HDO process showed the highest ROI (12%) and the shortest PBP (5 years) due to high yields of valuable heavy organics (32%) and MOAMON (24%). Direct HDO was found to be feasible with a positive NPV based on prices used in the assessment. Among the three processes investigated, the direct HDO process therefore appeared to be the most promising, and consideration should be given to further development and commercialization of this process. © 2019 The Authors. *Biofuels, Bioproducts, and Biorefining* published by Society of Chemical Industry and John Wiley & Sons, Ltd.

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Keywords: lignin valorization; lignin depolymerization; techno-economic analysis; lignocellulosic biorefinery; pyrolysis; hydrodeoxygenation; hydrothermal upgrading; biobased aromatics

Introduction

The need to decarbonize our economy is driving the development of viable and sustainable biorefining technologies that enable more efficient use of renewable feedstocks. To avoid competition with food supplies, second-generation lignocellulosic biomass is a preferred feedstock for future biorefineries.[1,2] There is also ongoing research on third-generation biomass – i.e. macro- and micro-algae.[3] Lignocellulosic biomass refers to inedible plant material mainly composed of cellulose, hemicellulose, and lignin. Effective utilization of lignin is considered an important means for developing economically profitable lignocellulosic biorefineries and reducing the carbon footprint.[4,5]

Lignin, which constitutes about 20–35% of dry biomass, binds cellulose and hemicellulose, and gives plant cell walls their rigidity.[4] It is the most abundant natural resource among the aromatics yet is largely unexploited for this purpose.[6] It has a lower oxygen content compared with cellulose and hemicellulose.[7] These properties make lignin an attractive feedstock for chemicals and fuels. Technologies for the conversion of carbohydrates (i.e. cellulose, hemicellulose fraction) to value-added products are relatively well established but lignin valorization processes are far less developed.[8,9] Large amounts of lignin (above 50 million tonnes) are currently produced, mainly as a byproduct of the pulp-and-paper industry.[4,10] In addition, with the development of lignocellulosic biorefineries for second-generation biofuel synthesis, significantly more lignin is expected to become available.[6,11]

Most lignin is currently used internally to deliver energy by combustion. However, the literature shows that 60% more lignin is produced than is needed to satisfy internal energy requirements.[12] As such, lignin is highly underutilized. Only a small amount of the lignin produced is used for purposes other than energy, mainly in the form of lignosulfonates, which are currently used as concrete additives, animal feed additives, agrochemical applications, dispersants, binders, adhesives, and resins.[13] These applications use lignin for their macromolecular structure and have low value and limited growth possibilities. The use of lignin for chemicals (aromatics) production is currently limited to vanillin.[14] However, lignin has high potential for a variety of applications and there is ongoing research to increase its commercial applications and value.[5] For example, the use of lignin for carbon fibers is currently being studied. This presents a macromolecular application with greater value.[6] There are also studies under way on the gasification of lignin into syngas, which can then be converted to chemicals and fuels such as methanol and dimethyl ether.[13] Due to the high content of aromatics in lignin, producing bio-based aromatics (cresols, catechols, guiacols, and syringols) from lignin is potentially attractive[5] and this application is considered in this paper.

Several studies have shown that the use of lignin co-products potentially contributes to better economic outcomes.[5,6,15–18] These studies compared the use of lignin to produce steam and electricity, to the use of lignin as lignosulfonates or soil amendment.[15,16] A report by the US National Renewable Energy Laboratory showed that costs for biofuel production from lignocellulosic-derived sugars can be reduced by pursuing opportunities to obtain value-added chemicals from lignin.[17] Another report by the Pacific Northwest National Laboratory estimated revenue improvements by utilizing lignin for mixed alcohols and aromatic chemicals production.[5] The well-known statement 'you can make anything from lignin except money' is therefore challengeable, although a large-scale market breakthrough still has to take place.[6,18]

Many different conversion technologies have been proposed for lignin depolymerization to bio-based aromatics. These methods can be broadly classified into pyrolysis, catalytic cracking, hydroprocessing, oxidation, hydrothermal processing, and acid / base catalyzed depolymerization.[19] Significant progress has been made on thermochemical approaches for lignin depolymerization such as pyrolysis[20–23] and chemocatalytic approaches involving the use of heterogeneous and homogeneous catalysts. An extensive overview of lignin valorization methodologies, catalyst developments, and key advances in this field is given in a number of reviews.[4,10,19,24–31]

Applying lignin depolymerization in an industrial context remains a major challenge. To this end, information on the potential technical and economic performance of new processes is key to increasing commercial adoption. However, assessing processes at an early stage of development (i.e., at lab / pilot scale) is inherently difficult due to the typically limited knowledge available. Nevertheless, methods exist to provide meaningful information regarding technological performance and economic viability. Despite inherent uncertainties, evaluating technologies at an early stage of development can be of great value. It provides insight into the potential of new technologies, and the drivers and targets for their further development. A typical assessment involves technical analysis based on process modeling coupled with an economic evaluation. Process modeling can be done with chemical engineering tools such as Aspen Plus. This approach has been applied to biofuels (i.e. bioethanol and biodiesel) and bio-based chemicals (i.e. lactic acid and succinic acid) production processes.[2,32–39]

Techno-economic analysis of different lignin depolymerization methods to evaluate and compare process options is largely lacking in the literature. In this study, three lignin conversion routes are assessed: (non-catalytic) lignin pyrolysis, direct hydrodeoxygenation (HDO) of lignin, and hydrothermal upgrading (HyThUp) of lignin.

Pyrolysis is a thermochemical conversion process that breaks down biomass using heat in the absence of oxygen. It is considered as a cost-effective way to utilize biomass.[40,41] Typical products are gas, liquid bio-oil, and solid char. The product distribution depends on the process conditions and feedstock used. Fast pyrolysis is generally considered an optimum route when aiming for the production of bio-oil, which can be easily stored and transported, and can be used for production of fuels and chemicals.[42] Various studies of lignin pyrolysis are available in the literature.[20,21,43–45]

Direct hydrodeoxygenation is a catalytic process involving making contact between lignin feedstock and hydrogen and heterogeneous catalyst.[4] Typically, elevated temperatures and pressures (> 300 °C and > 50 bar) are required.[46] The product oil yield and its chemical composition depend on the catalyst and reaction conditions applied. Numerous studies have been performed to identify the best catalyst system for high yield of aromatics and alkylphenolics, which are important high-value chemical intermediates.[4,47–49] Although solvents are generally used, solvent-free approaches have also been reported.[46,50–54] For large-scale applications, such solvent-free processes are preferred for economic considerations.[54]

Hydrothermal upgrading refers to the depolymerization of lignin in the presence of water at a medium temperature (200–350 °C) and high pressure (> 40 bar).[55,56] Catalysts can be used to optimize the conversion. Alkalis and noble metals (i.e. palladium, platinum, ruthenium, and rhodium) supported on either carbon, silica, and ammonia, are the most common catalysts applied.[56] Alkaline conditions are preferred to achieve a narrow product distribution and a high yield of phenolic compounds.[57]

The objective of this study is to give an ex-ante comparative techno-economic assessment of the three selected routes for lignin depolymerization to biobased aromatics. The results can be used to guide research and development by identifying early potential challenges and key cost drivers. The analysis also provides information on the potential performance of the three processes, thereby facilitating the selection of the process for further development.

Methodology

Approach

Figure 1 shows the approach taken in this paper. First, experimental data for each route, i.e., process conditions, raw materials, and product yields were collected. Market prices for raw materials and products were also gathered for the economic analysis. Next, the design basis was elaborated. A conceptual process design was made and the process models were developed. In this study, the Aspen Plus™ v8.6 flow-sheeting tool was used. Flowsheets of the routes were prepared with this, and mass and energy balances were determined. An economic assessment was performed based on this information, which involved capital and operating cost estimation. A discounted cash flow analysis was performed, and profitability was assessed using return on investment (ROI), payback period (PBP), and net present value (NPV) as key performance indicators. Finally, a sensitivity assessment was carried out for the parameters used to identify those that can influence the profitability.

Basis of design

In this paper, a plant size of 200 kt/year lignin input was selected. This is roughly equivalent to a 1 Mt/year lignocellulosic biorefinery, based on an assumed 20% lignin yield from dry biomass feedstock.[58] Eight thousand hours of plant operation per year were used. The plants were taken as stand-alone and greenfield with utility available at the factory gate. An n^{th} plant design was used, meaning that

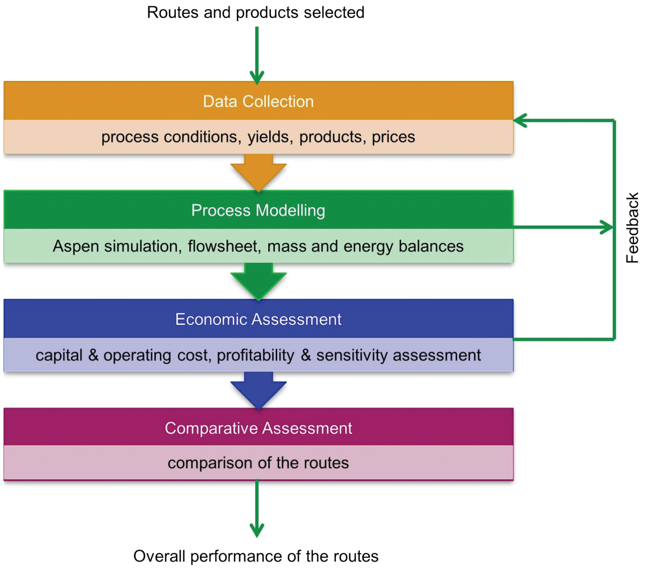

Figure 1. Schematic diagram of the approach taken in this analysis.

costs reflected a future time when the technology would be mature and several plants using the same technology have already been built and are operating. The higher costs for contingencies and longer startup times needed for the first-of-a-kind plants were therefore not included. The lignin source and conversion plant location were taken to be in northwest Europe. The processes considered here are all at an early stage of development. Accordingly, the process models developed do not reflect the current state of commercial availability but possible future plants as they would perform based on the current state of knowledge.

The process design was aimed at obtaining high-value product streams in sufficient quantity and without excessive separation effort. The processes were therefore designed to produce a limited number of mixed product streams containing classes of components. The product streams selected were mixed oxygenated aromatic monomers (MOAMON), light organics, heavy organics, and char. Unconverted lignin and water are also obtained as outputs. The main products are the mixed oxygenated aromatic monomers, which potentially have the highest added value.[50] It is a mixture of oxygenated aromatics including predominantly alkyphenols and monomeric phenols such as catechols, guaiacols, and syringols. The light organics stream contains a large variety of organics such as short alcohols and organic acids (e.g. methanol, acetic acid). The heavy organics stream is composed of high molecular weight organics such as oligomeric aromatics. Char is the solid product, mainly consisting of carbon. An overview of the lignin conversion routes is shown in Fig. 2.

Data inputs

This study was carried out as part of a large research program in the Netherlands, from which first-hand experimental data were obtained for the three routes.[59] For the lignin pyrolysis process, the lignin biorefinery approach (LIBRA) developed by ECN was shown to be promising in turning lignin into bio-oil and biochar while also satisfying the heat and power requirements of the process. Data from this process were considered in this study.[20,21,43,45] For the direct HDO process, data from a solvent-free process were used.[54] Solvent-free approaches are desired from a techno-economic perspective as extensive solvent recovery is avoided.[46,50–54] Finally, for the HyThUp process, a recent method of hydrothermal conversion of lignin and the *in situ* catalytic upgrading of the depolymerized lignin was considered.[57] Depolymerization and defunctionalization reactions take place in an aqueous solution of sodium hydroxide. Defunctionalization after depolymerization of lignin narrows down the number of different phenolic compounds.[57]

Figure 3 shows the experimental mass yields for the three processes based on the lignin intake for the selected product streams. In the pyrolysis process the full conversion of lignin is achieved. It has a relatively low yield (10%) of high value MOAMON, and a high yield (35%) of low-value char. Both direct HDO and HyThUp have high yield of valuable MOAMON (24% and 23% respectively) and heavy organics (32% and 20% respectively). Here, however, direct HDO has a high level of lignin conversion (96%), whereas HyThUp has a significant amount of unconverted lignin (34%).

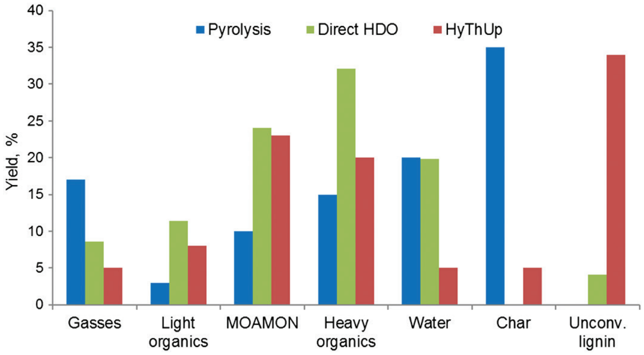

Figure 3. Reactor yield of products based on lignin intake for the three lignin conversion processes.

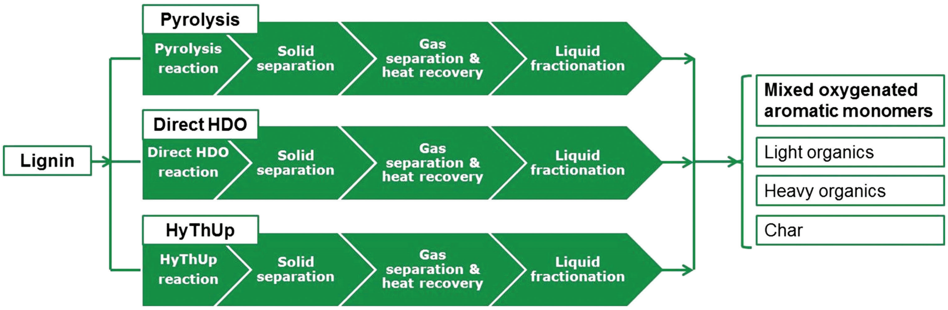

Figure 2. Overview of the lignin conversion routes selected in this paper.

The feedstock used in the experiments for pyrolysis and the direct HDO process is Indulin AT Kraft lignin. For hydrothermal upgrading experiments, Protobind 1000 soda lignin was used because of the incompatibility of the catalyst with the sulfur content of Kraft lignin. Both lignin types have been analyzed extensively for their composition and structure by Constant *et al.*[7] The type and quality of lignin used as feedstock are important for the end-product composition for all conversion processes. Lignin quality is also closely associated with the fractionation process used to obtain the lignin. Alternatively, for the lignin types mentioned, the use of high-purity organosolv lignin is possible for all three processes. However, the price of this type of lignin is likely to be higher than that of Kraft and soda lignin.

The prices of raw materials, utilities, and products used in the analysis are given and described in the supporting information, Table S1 in File S1. The separation of the product classes from each other is mostly achieved by distillation based on the differences in boiling points of the components. The boiling points of the components involved in the simulation are listed in the supporting information, Table S2, in File S1.

Process modeling

Process models were developed in Aspen Plus™ v8.6 (Aspen Technology, Inc., Houston, USA). The nonrandom two-liquid (NRTL) thermodynamic property method was used due to the presence of a non-ideal solution. The stream class of MIXCISLD was used, which is the default to introduce solid components in a simulation. There are two substreams of MIXED and CISOLID, where liquid and vapor components are present in the mixed substream, and solid components are present in the other. Continuous operation under steady-state conditions was considered. As lignin was not available in the databases of Aspen, a property database of the National Renewable Energy Laboratory was used, which is based on the work of Wooley and Putsche.[60] The main reactors were modeled with the RYield reactor type and the calculation was based on the yield of products with data from experiments (see Fig. 3). An important assumption made for all the processes was that the yield for the full-scale processes was the same as the yield in the lab-scale experiments. Further studies on reactor design and scale-up are needed to validate the yields for full-scale continuous processes that are currently not available.

To model the four product classes in Aspen Plus, model compounds were selected for each. For mixed oxygenated aromatic monomers, model compounds were determined based on the most dominant components seen from experimental data. These include guaiacol, catechol, syringol, phenol, and *m*-cresol. Light organics mainly include methanol and acetic acid. Methanol was taken as the representative compound. Heavy organics, which are mainly oligomeric aromatic substances, contain around 16 carbons, so the compound $C_{16}H_{16}O_2$, available in the Aspen database was taken as representative. Char, mainly consisting of carbon, was modeled as 100% carbon with solid C-Black, which gives a suitable representation of char.

The downstream equipment was modeled to achieve the separation of the product streams defined. Complete separation of solids from the liquid stream was assumed for simplification. Distillation units were modeled using the standard rigorous model available in Aspen Plus. The gas stream from the reactor was combusted to recover energy to be used in the process. Complete heat integration, including an assessment of the temperature level of the heat, was considered for calculating external utility requirements. The utility requirement of the continuous large-scale reactors was not available, and thus was not included, but the associated costs are considered in the economic calculations.

Economic analysis

The year 2012 was chosen as reference year because of the large fluctuations in raw material and product prices in more recent years. Historical data were corrected using the Chemical Engineering Plant Cost Index (CEPCI). When necessary, an exchange rate of 1.25 USD/EUR was used. For utilities of natural gas and electricity, prices from 2016 were used due to large fluctuations in the previous years (2012–2015). The price data are provided in the supporting information, Table S1, in File S1.

For the capital cost estimation, first the total installed cost of equipment was estimated based on the process model equipment and sizing information. Most estimations were made using the Aspen Process Economic Analyzer with only the investment costs of the sections involving solid processing estimated using the literature. Experimental data were obtained for batch autoclave reactors. In the upscale processes, continuous reactors will be likely used but the design of the continuous reactors is not known yet. Their investment costs were therefore estimated based on cost estimations given in literature sources. For the lignin pyrolysis process, the equation given by Bridgewater[42] (Eqn 1) was used to estimate the installed capital cost of the pyrolysis reactor system from the feed to the separated liquid oil:

$$\text{Installed capital cost fast pyrolysis system in M€} = 6.98 \times (\text{feed rate dry in t/h})^{0.67} \quad (1)$$

This equation for dry biomass pyrolysis was taken to be representative for lignin pyrolysis too. For the direct HDO process, the installed capital cost of the reactor section, including the hydrogen supply, was estimated from Jones *et al.*[61] This report also gives a scaling exponent of 0.65 for estimating the HDO section costs. In the HyThUp process, lignin is dissolved in aqueous solution, so it is a liquid phase operation. The reactor section was modeled in Aspen Plus considering one dissolution tank and four reactors in series with 4 h residence time. Their installed costs were estimated using the Aspen Process Economic Analyzer. Auxiliary equipment was estimated as 50% of the reactor costs. In the direct HDO and HyThUp processes, to estimate the cost of equipment for reaction outlet cooling, and for gas and solid separation from liquid, a scaling exponent of 0.67 was used as given in the literature.[62] For the pyrolysis process these are already accounted for in Eqn (1). The costs for the equipment for liquid separation and combustion of gasses were estimated using Aspen Process Economic Analyzer, with sizing results from the process simulation.

Once the scaled total installed costs of equipment (direct cost) were determined, indirect costs were estimated using factors from Peters *et al.*[63] for a solid-fluid processing plant. Contingency costs were calculated as 20% of total of direct and indirect costs seen as a typical value in the NREL reports.[64] As an *n*th plant design was used, this contingency value was considered appropriate, although for new technologies large contingencies would be needed. Fixed capital investment (FCI) was estimated by summing direct and indirect costs plus contingency. Working capital was taken as 15% of fixed capital investment to calculate the total capital investment (TCI). The resulting factors used in capital cost calculations can be found in the supporting information, Table S3, in File S1.

For the estimation of operating costs, first the variable operating costs that involve raw material and utilities costs were calculated using the mass and energy balances obtained from process models and prices given in the supporting information, Table S1, in File S1. Utility and catalyst requirements of the reactors are very much dependent on the design of the continuous large-scale reactor. As this information was unknown the following assumptions were made. For the utility requirement of reactors, additional costs of 5% of the lignin cost were considered. For the catalyst used in the direct HDO and HyThUp processes, as an initial assumption, annual catalyst costs were taken to be 10% of lignin cost. The labor costs were determined for a solid-fluid processing plant taken to be operated with 4.8 operators per shift position.[65] The number of shift positions was taken to be eight for pyrolysis, 12 for direct HDO, and 15 for hydrothermal upgrading process based on the complexity of the plant. A yearly wage of €41 600 was used as an average estimated wage for the Netherlands. Other operating cost items (i.e. maintenance, overheads, taxes and insurance, general expenses) were estimated based on percentages from known parameters using factors from Peters *et al.*[63] The factors used in these estimations can be found in the supporting information, Table S4, in File S1. Depreciation was calculated separately using a straight-line method with a 10-year recovery period.[63] This was added to the yearly operating costs in the discounted cash-flow analysis.

Revenues were calculated with the mass balance obtained from process models and using product prices given in the supporting information, Table S1, in File S1. With the capital costs, operating costs, and revenues determined, a discounted cash-flow analysis was performed based on the following economic assumptions and steps as described in Peters *et al.*[63] The tax rate was taken as 25%. The discount rate was set to an internal rate of return of 10% over a 20-year plant life, which is a typical value taken in, e.g., the National Renewable Energy Laboratory techno-economic analysis reports.[64] The construction period was set at 3 years with 30% of FCI spent in the first year, 50% in the second year, and the remaining 20% in the third year. In the final year of construction, working capital is invested to start the plant up. This working capital is recovered at the end of the plant life. The plant achieves 50% of production capacity during the first year of startup while incurring 50% of variable expenses and 100% of fixed costs. To assess the profitability, payback period, return on investment and NPV were calculated using the formulas described in the supporting information, based on Peters *et al.*[63]

As previously discussed, the bio-based processes described are still at early stage of development and there is a high level of uncertainty in the markets about the value of their products. A sensitivity analysis was carried out to identify the influence on changes of major raw materials and products prices on the NPV. The process models and the investment cost calculations are also associated with a large degree of uncertainty. The sensitivity of the NPV to the investment cost and discount rate were therefore also assessed. The parameters were varied by ±50% of the reference values. The effect on NPV of varying the production capacity was also assessed for each of the three processes. The capacity was varied in the range of 100–500 kt/year lignin input with 200 kt/year reflecting the base case. For variation of capital costs with scale, the six-tenth rule was applied. The operating costs were estimated for the different capacities as for the base case. Sensitivity to process parameters was not assessed because experimental data showing changes in process yields with changes in process parameters were not available.

Results and discussion

Process modeling

Lignin pyrolysis

The lignin pyrolysis process model is shown in Fig. 4. The reactor section was modeled with yield data from the section on data inputs above. In the Aspen model, the mixed oxygenated aromatic monomers stream is represented with the compounds guaiacol, catechol, and phenol. The distribution among them was modeled according to composition analysis.[45] Lignin is pyrolyzed in a circulating fluid bed pyrolysis unit at 500 °C where sand is used as heat carrier without the presence of a catalyst. From the reactor outlet stream, solids (char and sand) are removed in a cyclone and sent to a bubbling bed. At the bubbling bed, the separation of the large sand particles from smaller sized char is achieved. Char is obtained as a product stream. Reheated sand is recycled back to the pyrolysis reactor.

The gas reactor effluent separated with the cyclone is quenched with water to 30 °C. It is further cooled with electricity to 5 °C to increase the liquid yield. The liquid is separated from the gases in a flash vessel. The gas stream, comprising CO_2, CO and CH_4, is combusted for heat supply. The liquid stream undergoes several separation steps to separate the mixed oxygenated aromatic monomers, light organics, heavy organics product mix, and also to separate water.

First, the light organics (represented by methanol) are separated by distillation as it has the lowest boiling point (see supporting information, Table S2, in File S1). A light organics stream is obtained with 99.9%wt. recovery of methanol and with 99% mol purity. Second, complete separation of water from the other components is achieved in another distillation column. As the mixed oxygenated aromatic monomers have a density close to that of water, separation with, for example, a decanter is not possible. Finally, in the third distillation column, mixed oxygenated aromatic monomers are completely separated from the high-boiling heavy organics.

Direct HDO

The process model of the Direct HDO process is shown in Fig. 5. The reactor section was modeled with yield data from the section on data inputs above. The mixed oxygenated aromatic monomers stream is represented with the compounds *m*-cresol and phenol, which were considered the most dominant compounds.[54] These compounds were assumed to be equally distributed. In this route, feed lignin and hydrogen are fed to a depolymerization reactor operated at 400 °C, 150 bar, in

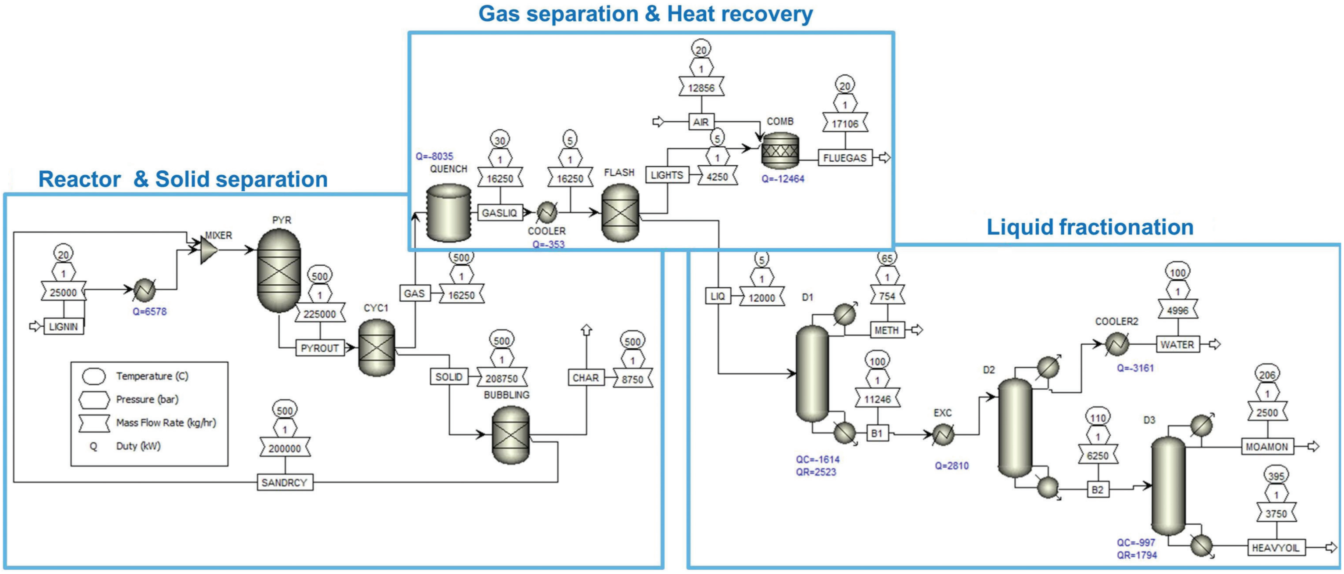

Figure 4. Aspen Plus™ model of the lignin pyrolysis process.

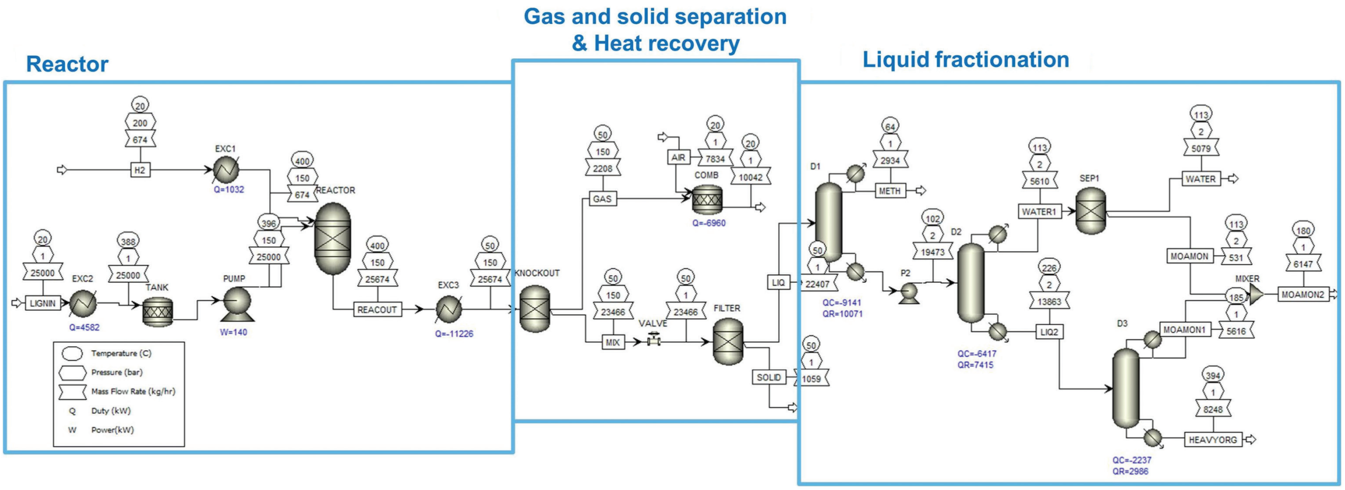

Figure 5. Aspen Plus™ model of the direct HDO process.

the presence of the catalyst (NiMo) without the use of a solvent. Hydrogen consumption is taken as 300 NL/kg. This is an early estimate and needs to be validated in experimental setups. Hydrogen is taken to be supplied to the plant at 200 bar. After reaction, the outlet stream is cooled to 50 °C and knock-out is done at high pressure. The gas stream is separated and combusted for heat supply.

The liquid product from the reactor is reduced in pressure making the residual lignin solidify. The solids are separated by filtration. This stream of solids consists of unconverted lignin and char, which are obtained together. The liquid stream undergoes several separation steps to separate the mixed oxygenated aromatic monomers, light organics, heavy organics product mix, and water.

First, the light organics, which are represented by methanol, are separated by distillation. Next, water is separated from the other components in a second distillation column. Additional separation is required to separate the mixed oxygenated aromatic monomers remaining in water. This is taken to be achieved with a novel hydrophobic membrane separator that selectively removes the organics from the aqueous stream. Such advanced membrane technology has been a topic of interest in recent research due to its high organic separation efficiency and ease of operation.[66-70] Further investigation of this technology and its possible application here is required for verification. This membrane unit is modeled with a black-box separator block. Finally, in a third distillation column, mixed oxygenated aromatic monomers are separated from heavy organics with high boiling points. The mixed oxygenated aromatic monomers separated earlier are combined with this stream to produce an overall mixed oxygenated aromatic monomers product stream. Note that this process is more complex than the lignin pyrolysis process due to the presence of hydrogen, and has more challenging requirements in separating water from the organics.

Hydrothermal upgrading

The hydrothermal upgrading process model is shown in Fig. 6. The reactor section was modeled with yield data from the section on data inputs above. In the Aspen Plus model, the mixed oxygenated aromatic monomers stream was represented with the compounds guaiacol, catechol, and phenol.[57] In this process, lignin is dissolved in an aqueous sodium hydroxide solution with a liquid-to-solid ratio of 5 kg/kg. The solution is sent to the depolymerization reactor, which is operated at 250 °C and 55 bar in the presence of a Pd/C catalyst.

After reaction, the outlet stream is cooled to 30 °C and pressure is reduced to 1 bar. Gas is separated in the knock-out drum and combusted for heat recovery. The resulting slurry is sent to a filter to separate the solid char from the liquid. Char is considered a product stream. Sulfuric acid is added to the resulting liquid stream, to reduce the pH and thereby induce the precipitation of unconverted lignin. This is then removed by filtration from the liquid stream. The sulfuric acid reacts with the sodium hydroxide resulting in sodium sulfate salts. The resulting liquid stream undergoes several separation steps to separate the mixed oxygenated aromatic monomers, light organics, heavy organics product mix, and water.

In the process design proposed, methyl isobutyl ketone (MIBK) solvent is used to extract phenols from the liquid stream. Separation of MIBK from phenol is achieved by distillation. The recovered MIBK is sent back to the

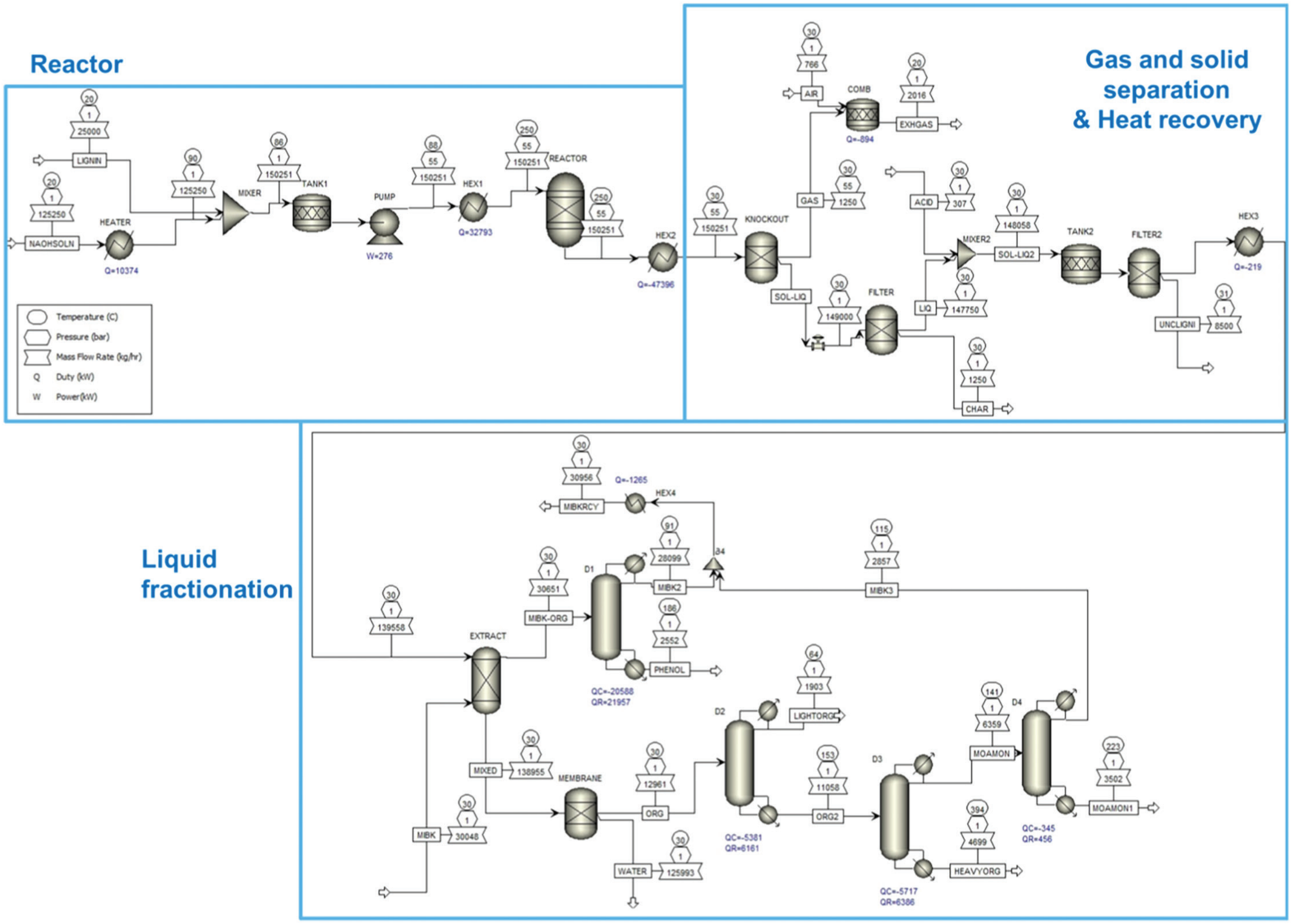

Figure 6. Aspen Plus™ model of the hydrothermal upgrading (HyThUp) process.

extraction column. Note that the liquid stream contains a significant amount of water (90 wt%). With the mixed oxygenated aromatic monomers having a density close to water, separation with a decanter, for example, was not possible. To avoid distillation, as it is very energy intensive, a novel hydrophobic membrane separator was considered to separate water, similar to the approach followed in the direct HDO process. The water stream contains sodium sulfate salts and is sent to the wastewater treatment unit.

From the organics stream, first the light organics are separated by distillation. Next, separation of mixed oxygenated aromatic monomers from heavy organics is achieved in a second distillation column. The distillate from this column still contains some MIBK, which is separated in an additional distillation step from the remaining mixed oxygenated aromatic monomers stream and recycled. The mixed oxygenated aromatic monomers stream and the phenols separated earlier by extraction can be combined to make an overall mixed oxygenated aromatic monomers product stream.

As shown in Fig. 6, considerable separation efforts are required, mostly due to the presence of a fast flow rate of water in the system. Further experimental studies are required to evaluate potential avenues to increase lignin conversion and / or the recyclability of the unconverted lignin. Salts are also produced in this process from the reaction of sodium hydroxide with the acid. The influence of the salts on the separation performance was not considered here and needs to be assessed in further studies.

Mass and energy balances

Mass balances for the three lignin conversion processes are shown in Table 1. Inputs into the system are the raw materials entering the process. Hydrogen is used in the direct HDO process. Aqueous sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) are used in the HyThUp process.

Table 1. Mass balances of the three lignin conversion processes in kg h^{-1}.

	Pyrolysis		Direct HDO		HyThUp	
	Input	Output	Input	Output	Input	Output
Raw materials						
Lignin	25 000	—	25 000	—	25 000	—
Hydrogen	—	—	674	—	—	—
Aq. NaOH	—	—	—	—	125 251	—
H_2SO_4	—	—	—	—	307	—
Air	12 856	—	7834	—	766	—
Products						
Light organics	—	754	—	2934	—	1903
MOAMON	—	2500	—	6147	—	6054
Heavy organics	—	3750	—	8248	—	4699
Char	—	8750	—	—	—	1250
Waste water	—	4997	—	5079	—	125 993
Unconv. lignin	—	—	—	1059	—	8500
Flue gas	—	17 106	—	10 042	—	2016
Loss	—	—	—	—	—	909

Outputs are the product streams after separation. For the combustion of gasses produced during reaction, air is used and flue gas is emitted. Complete separation of solid products from the liquid was assumed in all cases. The amounts lost are given in Table 1 and correspond to the amount lost during MIBK recycling. They are mainly composed of water (87%) and light organics. For the HyThUp process, a large amount of waste water is seen in Table 1 due to large water requirements for dissolving lignin. In a more advanced design water could be separated from its contaminants thereby significantly reducing water consumption and waste water production but at the cost of increased energy use. More information about contaminants is required for such an assessment.

When comparing the mass balances of the three processes given in Table 1, there is a great variation in the flow rate of final product streams in accordance with the different reactor yields given in Fig. 3. The direct HDO process produces the largest quantity of light organics, MOAMON, and heavy organics. This is important for the economic analysis as MOAMON and heavy organics have the highest economic value. In the pyrolysis process, char is the product that is produced most (8750 kg/h); however, this has a relatively low value. Compared with the other two processes, significantly less valuable MOAMON and heavy organics are produced in this process (2500 kg/h MOAMON compared with more than 6000 kg/h in the other two processes). There is significant amount of unconverted lignin in the HyThUp process (8500 kg/h), resulting in lower production of valuable products MOAMON and heavy organics compared with the direct HDO process.

In the pyrolysis and direct HDO processes, the liquid product streams could be well separated (> 99%) with high purity (> 99%). In the HyThUp process, separation was more demanding. Light organics were obtained with 95% recovery and > 99% purity. Heavy organics were obtained with 94% recovery with > 99% purity. MOAMON was obtained with > 99% recovery and at 94% purity because some heavy organics were extracted together with phenol. At this early stage of development, model compounds were used to represent products in Aspen Plus. In reality, due to presence of many more compounds in each product class, the separation task will be more complex. As the technology develops further, detailed design studies will be required to evaluate pathways to obtain product classes with a high level of purity.

The energy balances of the processes are shown in Table 2. The gross heating duty represents the total amount of energy to be supplied for heating process streams. The gross cooling duty represents the energy that needs to be removed by cooling to match the set process temperatures. In the analysis, the possibility of total heat integration was considered and utility requirements were calculated based on that. Optimization using pinch analysis was not done but the temperature levels of the exchanging streams were adjusted to achieve a minimum approach temperature of 10 °C. External utility requirements of the three processes are given in Table 3.

Table 2. Energy balance of the three lignin conversion processes.

	Pyrolysis	Direct HDO	HyThUp
Gross heating duty (MW)	13.7	26.1	78.1
Gross cooling duty (MW)	14.1	29.0	80.9

Table 3. External utility requirements of the three lignin conversion processes, assuming full heat integration.

	Pyrolysis	Direct HDO	HyThUp
Electricity (kW)	353	140	495
Cooling water ($t\,h^{-1}$)	374	348	1039
Natural gas (MW)		1.8	31.5

For all three processes, the gas stream from the reactor were combusted to supply heat internally. A large amount of the heat available from the cooling of the reactor effluent, which is 8 MW for pyrolysis, 11 MW for direct HDO, and 47 MW for HyThUp, was also considered to cover the heating demands of the processes. The heat available in the pyrolysis process was found to be sufficient to cover the heating demands of the process. The net net heating demand of this process, after heat integration, was therefore found to be 0. For the direct HDO process, part of the heating demand of third distillation column's reboiler needed to be supplied by utility because the temperature level of the streams available for heating were not suitable. A fired heater using natural gas as fuel was considered as an external utility due to the high temperature requirement (> 394 °C). Similarly, for the HyThUp process, the heating demand of the third distillation column's reboiler plus part of the reactor feed heating needed to be supplied by a fired heater. The net heating demands of the direct HDO and HyThUp processes were calculated in Aspen Plus models as 1.8 MW and 31.5 MW respectively (see Table 3). The higher demand for the HyThUp process is due to the high separation efforts required as explained in the previous section.

The net cooling demand, considering total heat integration for the processes, was calculated as 12.9 MW, 11.7 MW, and 35.2 MW for the pyrolysis, direct HDO, and HyThUp processes respectively. The required cooling water amounts to supply the cooling demand for the three processes were calculated in the Aspen process models and are given in Table 3. As expected from Table 2, the cooling water requirement was the highest for the HyThUp process. This was mainly due to the high flow rate of water in the system. The model was developed to save energy by using extraction and novel separation technologies such as membrane units but the total amount used was still high. Finally, additional excess heat can arise by incinerating the unconverted lignin in the HDO (~8 MW) and the HyThUp (~64 MW) processes directly.

Economic analysis

Capital cost estimation

For the pyrolysis process, the installed capital cost of the pyrolysis reactor system from feedstock to separated liquid oil (all solid processing) was calculated as M€60. For the downstream operation involving combustion of gases and liquid product separation, the Aspen Process Economic Analyzer was used. The installed equipment costs for this section were calculated as M€15, giving a total of M€75 for the whole system (see Table 4). For the direct HDO process, the installed capital cost of the reactor section involving solid processing was estimated as M€47, using the literature described in methodology section. The installed capital cost of the reaction outlet cooling and gas separation was estimated as M€4. This gives an overall cost of M€51 for the reactor section. The cost for the equipment for liquid separation and combustion of gases was estimated, using the Aspen Process Economic Analyzer, as M€40, giving a total installed equipment cost of M€91 (Table 4).

In the HyThUp process, because the lignin is dissolved in an aqueous solution the reaction happens in liquid phase, contrary to other two processes. The installed cost of the reactor section was estimated, using the Aspen Process Economic Analyzer, as M€22. The literature described in methodology section was used to estimate the cost of equipment for the reactor outlet cooling, gas / liquid, and solid / liquid separation. Two solid separation steps (char and unconverted lignin) were considered. The installed costs for this section were estimated as M€12, giving a total of M€34 for the reactor section. The costs of the equipment for liquid separation were estimated, using the Aspen Process Economic Analyzer, as M€68. The total installed equipment cost for the whole process is M€102 (Table 4).

The indirect costs and contingency costs were then calculated from the total installed equipment costs (direct plant costs). The breakdown of the capital cost estimation and the resulting FCI and TCI for the three lignin conversion processes are given in Table 4. In the direct HDO process, due to the greater complexity of separation units, a larger investment than pyrolysis process was obtained (TCI M€163 compared to M€135). In the HyThUp process, there is a lower capital cost requirement for the reactor section compared to other processes, due to liquid phase operation. However, due to the presence of a large amount of water in the system, the liquid separation

Table 4. Capital cost estimation of the three lignin depolymerization processes.

	Pyrolysis (M€)	Direct HDO (M€)	HyThUp (M€)
Installed cost reactor section	60	51	34
Installed cost fractionation	15	40	68
Total direct plant cost	75	91	102
Indirect cost	22	27	30
Contingency	20	24	26
Fixed capital investment (FCI)	117	142	158
Working capital	18	21	24
Total capital investment (TCI)	135	163	182

section is very complex and demands a series of separation steps resulting in higher capital requirement compared to other processes. As a result, the HyThUp process has the overall highest capital cost (TCI M€182).

Operating cost estimation

First, variable operating costs that involve raw material and utilities costs were calculated (shown in dark and light green respectively in Fig. 7). Raw material cost contributes the most to the total operating costs for all three processes. Lignin costs were calculated as 50 M€/year, which is the same for all three processes because they were modeled using the same 200 kt/year lignin input. For the direct HDO process, hydrogen used in the process has a significant effect on the costs (14 M€/year). For the HyThUp process, the costs of the raw materials, sodium hydroxide and sulfuric acid, are not significant but the higher utility demand due to the complexity and the number of separation units resulted in higher utility costs for this process (Fig. 7).

Fixed costs were calculated for the three processes as shown in blue in Fig. 7. The HyThUp process was found to have the highest fixed costs (26 M€/year) due to its higher investment costs and higher plant complexity. However, the direct HDO process was found to have the highest operating costs (96 M€/year) due to the large impact of hydrogen cost on this process. Depreciation was calculated separately and not included in the operating costs shown in Fig. 7.

Profitability analysis

Revenue breakdowns for the three lignin conversion processes are shown in Fig. 8. The pyrolysis process has the lowest revenues due to its low yield of the most valuable mixed oxygenated aromatic monomer (MOAMON) product stream. A significant amount of char is produced in this process; however, from an economic point of view it does not provide high revenues due to its lower price. MOAMON, char, and heavy organics contribute similarly (24-29 M€/year) to the total revenue of the pyrolysis process.

The revenues for the HyThUp process are high (109 M€/year) due to its high yield of the target product, MOAMON. MOAMON is the major contributor, with 70% of total revenues. Heavy organics form the rest of the contribution, with light organics and char only contributing marginally (4–5% each).

The direct HDO process shows the highest revenue (131 M€/year) due to its high yield of both MOAMON and heavy organics. MOAMON contributes 54% of total revenue and heavy organics contributes 40% of total revenue. A significant quantity of light organics is produced

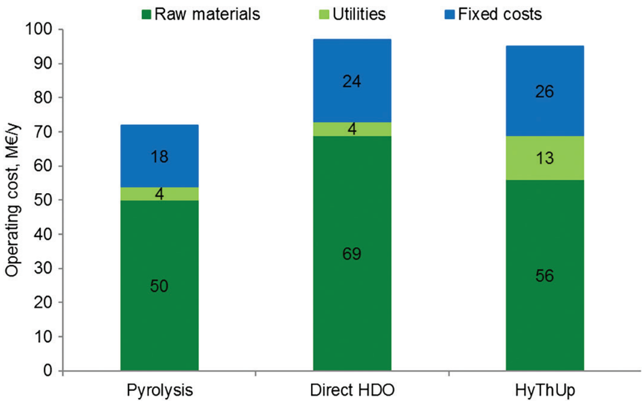

Figure 7. Total operating costs (without depreciation) breakdown for the three lignin conversion processes.

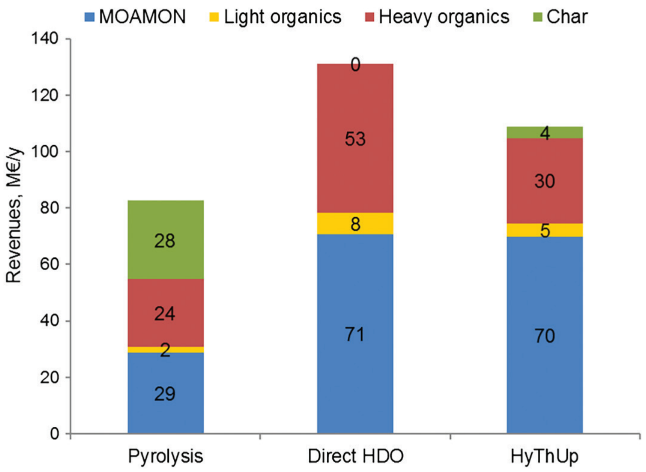

Figure 8. Annual revenues for the three lignin conversion processes.

in this process (half of MOAMON by mass, Table 1) but due to its lower value it only accounts for 6% of the contribution to revenue.

An overview of the economic results for the three lignin conversion processes is given in Table 5. The pyrolysis process showed the lowest investment and operating costs. However, the revenues are the lowest due to the low yield of the main product, MOAMON, as discussed above. This resulted in a low but still positive return on investment (2.2%) and a long pay-back period (13 year). With the economic parameters used in this study, a negative NPV was obtained indicating the economic infeasibility of the process under the conditions in this study.

The direct HDO process showed a slightly higher investment than pyrolysis due to the more demanding downstream separation of the product streams. Operating costs were the highest, mainly due to the significant cost of hydrogen raw material. This process has the highest revenues due to the high yield of heavy organics and MOAMON as also discussed above. This enables it to have the highest return on investment of 12% and the shortest pay-back period (5 years), which is considered to be very promising. With the economic parameters used in this study, it gives a positive NPV, showing the feasibility of the process.

The HyThUp process has the highest investment costs due to the requirement for a large amount of aqueous solution to be fed with the lignin, resulting in a significant separation requirement. This process also has high operating costs due to the high fixed costs because of greater plant complexity. This process also has the greatest utility requirements due to the high flow rate of water in the system, as explained above. Although, this process has large revenues (31% more than pyrolysis), this is not high enough to achieve a positive NPV. The return on investment (1.7%) and payback period (14 year) calculated for this process are slightly worse than those calculated for the pyrolysis process.

Table 5. Overview of economic results for the three lignin conversion processes.

	Pyrolysis	Direct HDO	HyThUp
Total capital investment (M€)	135	163	182
Operating costs (without depreciation) (M€ year^{-1})	72	96	95
Revenues (M€ year^{-1})	83	131	109
NPV (M€)	–72	47	–106
Return on investment (ROI) (%)	2.2	12.1	1.7
Pay-back period (PBP) (year)	13	5	14

Sensitivity analysis

To assess the impact of variations on economic performance, a sensitivity analysis was carried out for the prices of major raw materials and products. The sensitivity of the NPV to the investment cost and discount rate was also assessed. The results are presented in Figs 9-11 for pyrolysis, direct HDO, and the HyThUp process, respectively.

For the pyrolysis process, the lignin price appears to have the greatest impact on the results for the parameters studied (see Fig. 9). The influence of char price was also studied due to the high char yield from this process. It was found to have a similar effect with the variation of MOAMON price. Figure 9 shows the range of char price 200–600 €/tonne. There is a large uncertainty in char price depending on the application of char, varying up to 1000 €/tonne for carbon black, which would give a NPV of M€186. The effect of the MOAMON price is lower than in the other two processes due to the lower yield of this product in the pyrolysis process. A negative NPV was obtained with the base economic parameters used in this study. The NPV becomes positive when either the TCI is lowered by ~30% or the lignin price by ~20% or the MOAMON and char price is increased by ~40%. Variations in the prices of heavy organics and in the discount rate do not result in favorable economic outcomes.

For the direct HDO process, the prices of MOAMON and heavy organics have a large influence due to the large yields of these products in the direct HDO process (see Fig. 10). The lignin price also has a large impact. The hydrogen price appears to have a minor impact on the results. With the

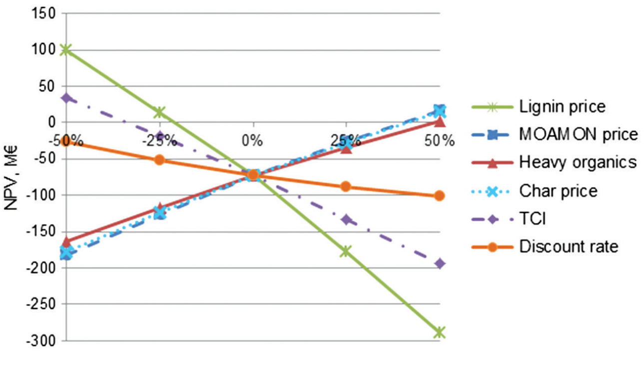

Figure 9. Sensitivity analysis for pyrolysis process.

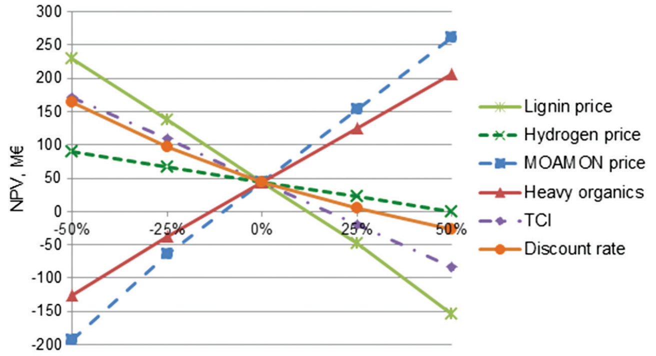

Figure 10. Sensitivity analysis for direct HDO process.

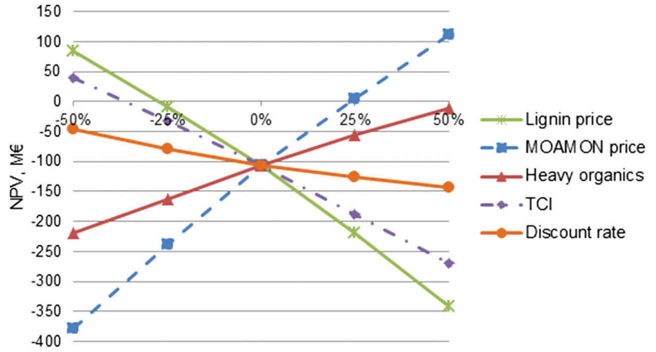

Figure 11. Sensitivity analysis for HyThUp process.

base economic parameters used in this study, a positive NPV was obtained. Increasing the TCI by ~20% or lignin price by ~10% or decreasing the MOAMON price by ~10%, and heavy organics by ~15%, results in a negative NPV and the process becomes economically infeasible.

As for the HyThUp process, MOAMON and lignin prices are highly influential (see Fig. 11). The heavy organics price has a lower influence in this process than in the direct HDO process due to the lower yield of this product. With the base economic parameters used in this study, a negative NPV was obtained. The NPV becomes positive when either the TCI is about 35% lower or the lignin price is about 25% lower, which is similar to the results obtained for the pyrolysis process. However, increasing the MOAMON price by ~25% is sufficient to make the route economically viable.

Overall, the sensitivity analysis shows that a variation of about 25% can influence whether the processes are feasible or not. A 25% reduction in the quite uncertain lignin price (250 €/tonne) can result in all processes having a positive NPV. For the pyrolysis process, the break-even point (NPV = 0) corresponds to a lignin price of 198 €/tonne, and for the hydrothermal upgrading process 181 €/tonne.

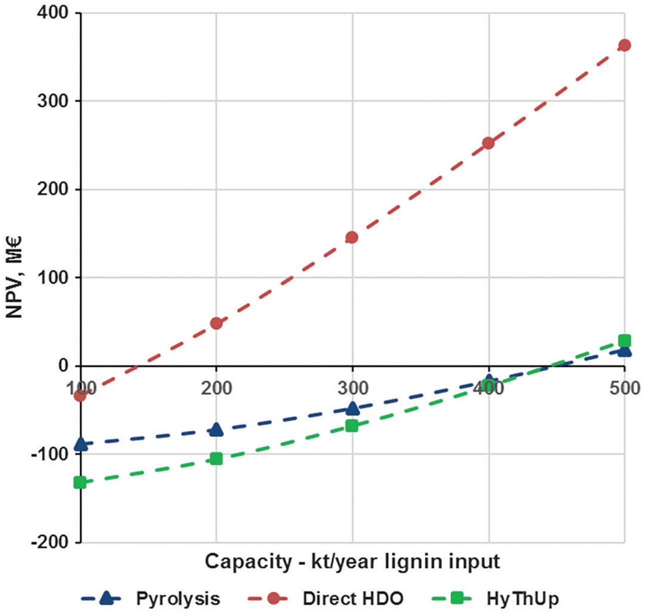

Figure 12. Sensitivity analysis on lignin input capacity variation for all processes.

Figure 12 shows the effect of varying the capacity of lignin intake on the NPV. The results show that all three processes benefit from economy of scale. The base case is 200 kt/year of lignin input. At a lower capacity of 100 kt/year, all three processes have negative NPV. The direct HDO process benefits the most from economy of scale and remains the most profitable process. Figure 12 suggests that the pyrolysis process benefits less from economy of scale than the HyThUp process because the HyThUp process has higher revenues than the pyrolysis process and the impact of its higher investment cost becomes less pronounced as capacity increases. They both break even around 450 kt/year of lignin input. At a higher capacity, the HyThUp process becomes slightly more profitable than the pyrolysis process.

Conclusions

This study assessed the performance of the pyrolysis, direct hydrodeoxygenation, and hydrothermal upgrading routes for the conversion of lignin into bio-based aromatics. The direct HDO process was found to be more complex than the lignin pyrolysis process due to the use of hydrogen and more challenging separation requirements. The HyThUp process had the most demanding downstream processing, mostly due to the presence of a large flow rate of water in the system. Accordingly, the energy requirement of this process was the highest. In terms of economics, the HyThUp process showed the highest capital cost (M€182).

For the direct HDO process, due to the greater complexity of the separation tasks, it was estimated that the investment costs would be higher than those for the pyrolysis process (M€163 compared to M€135).

The direct HDO process appeared to be the most promising due to the high revenues (58% more than pyrolysis). The operating costs were the highest among the three processes (34% more than pyrolysis) due to the use of hydrogen. However, because of its high yield of the target product, MOAMON (24%), and of valuable heavy organics (32%), positive economic results were obtained. The payback period of 5 years and return on investment of 12% can be considered attractive for investment. Negative NPVs were calculated for the pyrolysis and HyThUp processes, suggesting economic infeasibility. The price of lignin and MOAMOM were found to have the largest impact on the NPV. A decrease of 25% in the quite uncertain lignin price can result in a positive NPV for all processes. Increasing the capacity over 450 kt/year (base case is 200 kt/year) can result in positive NPV for the pyrolysis and HyThUp processes.

Experimental studies should focus on the process challenges that were identified, such as the evaluation of potential avenues for increasing lignin conversion and the selectivity towards monomeric bio-based aromatics. Further process studies should aim for a more detailed description of the reactor and separation sections and should reflect full-scale performance. Research into less energy-intensive separation technologies to separate water from organics, more detailed assessment of the heat integration, and for the HyThUp process investigation of water recycling, are also important. This ex-ante techno-economic assessment provides valuable information to steer future experimental studies and provide direction for the further development and commercialization of lignin depolymerization technologies for bio-based aromatics.

Acknowledgements

This research was performed within the framework of the Dutch research program CatchBio. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands, Ministry of Economic Affairs, and the Netherlands Ministry of Education, Culture and Science (Project number 053.70.381). Additional funding from the Netherlands Ministry of Economic Affairs, as part of ECN's biomass research program is acknowledged. The authors acknowledge Paul de Wild from ECN part of TNO, Erik Heeres from the University of Groningen and Daan van Es from Wageningen University and Research for the information and data provided.

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