

Continuous-flow production of petroleum-replacing fuels from highly viscous Kraft lignin pyrolysis oil using its hydrocracked oil as a solvent

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ABSTRACT

The development of solvent-free lignin pyrolysis processes is highly desirable, because these processes would allow the depolymerized product to be used directly as a renewable energy source and chemical feedstock, without removal of solvents. However, this product is typically highly viscous and cannot be used in continuous-flow reaction systems. In this study, lignin pyrolysis oil was prepared from Kraft lignin using bench-scale fixed-bed batch pyrolysis and then hydrocracked to produce less-viscous liquid products. Oligomers were degraded into smaller molecules via reactions involving hydrogen (hydrocracking) using CoMo/H β and CoMo/Al₂O₃ as catalysts. A low viscosity of 21 cP, a liquid yield of 76.6%, and a low coke yield of 1.6% were successfully attained using a reaction temperature of 400 °C, a reaction time of 60 min, and the CoMo/H β catalyst. Thus, these conditions were selected to achieve the highest liquid yield with sufficient fluidity, although the lowest viscosity of 3.2 cP was achieved after 240 min. When 30 wt% of the resulting hydrocracked oil was used, it dissolved sticky raw lignin pyrolysis oil, significantly reducing its viscosity from 751 cP to 111 cP, which is sufficient to ensure flow in a typical petroleum pipeline. Using the hydrocracked/raw lignin pyrolysis oil mixture, the proposed continuous-flow hydrodeoxygenation successfully produced petroleum-replacing deoxygenated fuels.

1. Introduction

Global warming and the depletion of fossil fuels are major problems that have attracted social and technical interest [1,2] and must be quickly solved to fulfill energy demands and reduce greenhouse gas production. Various methods for sustainably producing the energy and chemicals that support the global economy have been proposed. In this context, biomass represents a promising resource for the production of energy and chemicals, both of which are currently derived from petroleum [3]. Although lipid-based biodiesel and sugar-based bioethanol are mass-produced and used as petroleum-replacing fuels, inedible biomass feedstock has also been studied to avoid conflicts with the food supply. In particular, lignocellulose, including wood and grass, has been studied as an inedible biomass source that can supply sugars and other carbon-rich chemicals [4–6]. The saccharification of the cellulose in lignocellulose for producing sugar-based bioalcohols has been a major

target for the development of lignocellulose-based biofuels. Additionally, lignin, which is a waste product in cellulose-focused processes, has also attracted interest for its potential to improve the economic feasibility of biorefinery processes and as a replacement for petroleum or producing valuable chemicals.

The production of fuels and chemicals from lignin has been studied using chemical processes, including catalytic and thermal depolymerization methods [7–10]. Although lignin pyrolysis has been reported to be difficult [8], it does not require any solvent, which enables direct utilization of the depolymerized products as feedstocks for further processes, unlike in solvent-diluted catalytic depolymerization [11,12]. Petroleum-replacing fuels can also be produced from lignin pyrolysis oil, but deoxygenating these fuels requires upgrading processes, which are far more difficult than upgrading lignocellulose pyrolysis oil [13,14].

Lignin pyrolysis oil can be upgraded to petroleum-replacing

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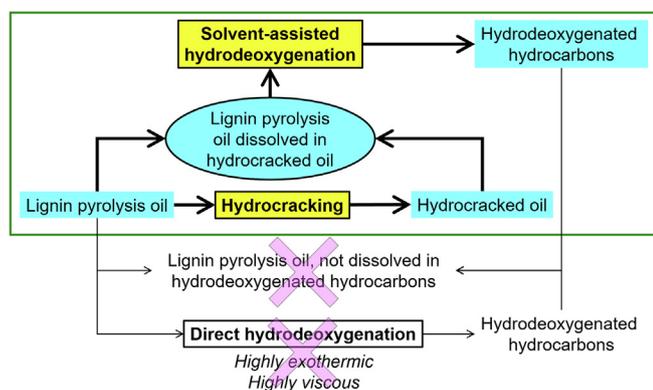


Fig. 1. Upgrading lignin pyrolysis oil using its hydrocracked oil.

deoxygenated hydrocarbon fuels by hydrodeoxygenation (HDO). The catalytic upgrading of biomass-derivatives has been reported using supported metals, including Pt [15], Ru [13,14], Ni [16], and Fe-Re [17], and Mo-based catalysts [18–22], and deoxygenation has successfully been achieved. However, coking rapidly deactivates HDO, which hinders its scale-up [14,23,24]. The importance of the support material has also been demonstrated [25,26]. Although many catalytic processes have been proposed for the HDO of biomass pyrolysis oil [13,27,28], the significant heat released during HDO and the sticky nature of lignin pyrolysis oil both hinder stable continuous-flow HDO processes [8]. Because lignin pyrolysis oil is significantly viscous, solvents like alcohols have been used to stably operate lignin conversion [29]. Although solvents can facilitate the HDO of lignin pyrolysis oil, the resulting HDO products are difficult to characterize, and the diluting the lignin pyrolysis oil complicates process scale-up.

In this study, to avoid the use of highly viscous lignin pyrolysis oil as a reactant, we investigated the hydrocracking of this oil to reduce its viscosity by degrading the oligomers and highly functionalized compounds that it contains (Fig. 1). The less viscous liquid formed after degradation can also be used as the solvent for raw lignin pyrolysis oil and further used in the continuous-flow HDO process. No solvent is required to dissolve the lignin pyrolysis oil using this strategy, which can avoid the need to further purify the final HDO products. Supported CoMo catalysts were selected for the hydrocracking of lignin pyrolysis oil because they have previously been used for catalytic hydrocracking of highly viscous vacuum residue [30].

2. Experimental

2.1. Materials

Kraft lignin was purchased from Sigma-Aldrich (Milwaukee, Wisconsin, USA), and its pyrolysis oil was prepared using a bench-scale fixed-bed batch reaction system, as described in a previous study [31]. Briefly, the fast pyrolysis of Kraft lignin (100 g) was performed at 500 °C under a N₂ flowing at 600 mL/min. The vaporized lignin pyrolysis oil was collected using four condensers, one cooled by the ambient air and the others cooled to –30 °C. The prepared lignin pyrolysis oil was extracted using dichloromethane to remove water and solid particles. The alumina-supported CoMo catalyst (CoMo/Al₂O₃) was purchased from Strem Chemicals (Newburyport, Massachusetts, USA) and sieved to 150 μm. Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), ammonium molybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O, ruthenium chloride hydrate (RuCl₃·xH₂O), and dimethylsulfide (DMS, CH₃SSCH₃) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Hβ was purchased from Vision Chemical (Aurora, Colorado, USA). Tetrahydrofuran (THF) was purchased from Honeywell (Charlotte, North Carolina, USA).

2.2. Catalyst preparation and characterization

The wet impregnation method was used to prepare CoMo/Hβ. Cobalt nitrate hexahydrate (2.8 g) and ammonium molybdate tetrahydrate (3.3 g) were dissolved in a mixture of Hβ (17.6 g) and deionized water (100 mL, 18.2 MΩ·cm). The mixture was stirred for 1 h and then dried at 60 °C using a rotary evaporator. The prepared catalyst was sieved to 150 μm, reduced under a flow of 5 vol% H₂ in Ar at 400 °C for 3 h, and then passivated under a flow of 1 vol% O₂ in N₂ for 1 h at room temperature. The elemental compositions of the catalysts were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES, iCAP 6000 Series, Thermo Fisher Scientific, Waltham, Massachusetts, USA). The catalysts were also observed using transmission electron microscopy (TEM, Tecnai F20 G2, Thermo Fisher Scientific, Waltham, Massachusetts, USA) equipped with energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD, D8 Advance, Bruker, Billerica, Massachusetts, USA). The pore structures of the catalysts, including Brunauer-Emmett-Teller (BET) surface areas and Barrett-Joyner-Halenda (BJH) pore size distributions, were measured using N₂ physisorption (ASAP 2020, Micromeritics, Norcross, Georgia, USA).

2.3. Characterizing the reactant and liquid products

The lignin pyrolysis oil reactant and the liquid products were characterized by gas chromatography/mass spectrometry (GC/MS, Agilent 78900A with 5975C inert MS XLD) using an HP-5MS capillary column (60 m × 0.25 mm × 250 μm) with a flow of He (50 mL/min). The column was maintained at 40 °C for 5 min, and then heated from 40 to 275 °C at heating rate of 7 °C/min. The detector and injector were heated to 300 °C. The product was diluted using a four-times larger volume of acetone for the measurement. Elemental analyses were performed using a Flash 2000 series CHNS organic elemental analyzer (Thermo Scientific) at the Korea Institute of Science and Technology (KIST) Advanced Analysis Center (Seoul, Korea), while oxygen analyses were performed using a Fisons Instruments EA 1108 analyzer (Thermo Scientific). The heating values of the reactant and products were calculated using the Dulong equation: higher heating value (HHV, MJ/kg) = 33.742 × [C] + 143.905 × ([H] – [O]/8) + 9.396 × [S], where [C], [H], [O], and [S] are the elemental mass fractions as measured by elemental analysis [32]. The moisture contents of the oils were measured using a Karl Fischer MKV-710 moisture titrator with the addition of Hyranal-Composite-5 and a 75:25 (v/v) mixture of methanol and chloroform as the solvent. The quantity of coke formed during the reaction was determined by thermal gravimetric (TG) analysis using an SDT Q600 instrument (TA Instruments) under flowing air. The molecular weight distributions of the lignin pyrolysis oil reactant and liquid products were determined by gel permeation chromatography (GPC, Agilent 1200 HPLC) equipped with two Shodex LF-804 columns and an ultraviolet (UV) detector measuring at 270 nm. In a typical GPC characterization, 20 mg of the liquid sample, which included the lignin pyrolysis oil and its converted products, was fully dissolved in 20 mL of THF. The column was operated at room temperature and eluted with THF flowing at 1.0 mL/min. The GPC results were calibrated against the ReadyCal polystyrene standard set (Aldrich, 250–2,000,000 g/mol). Rheological parameters were measured using an RM 100 touch device (Lamy Rheology Instruments, Lyon, France) with a rotating spindle (CP 6005-16.6). Typically, the representative viscosity of each liquid sample was measured at 25 °C at a shear rate of 50 s^{–1}.

2.4. Hydrocracking of lignin pyrolysis oil

The lignin pyrolysis oil was hydrocracked in a 50-mL high-pressure batch reactor and the products were characterized as depicted in Fig. 2. Typically, the lignin pyrolysis oil (5 g), the catalyst (0.5 g, CoMo/Al₂O₃ or CoMo/Hβ), and DMS (0.05 g) were loaded into the reactor, which

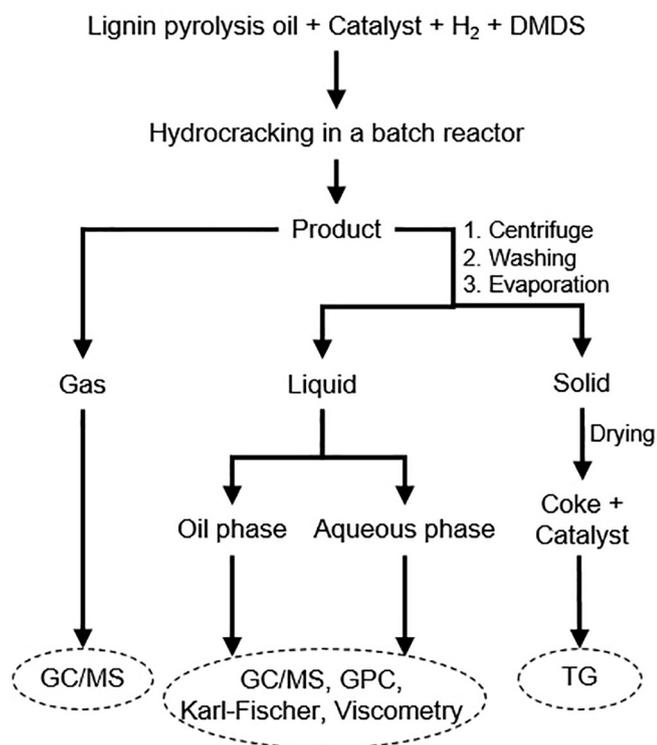


Fig. 2. Characterization of hydrocracked lignin pyrolysis oil.

was then pressurized with H_2 (100 bar) at 30 °C, and heated to the desired reaction temperature (300–400 °C) at 10 °C/min with stirring at 200 rpm. DMDS was used to maintain the sulfur content in the reaction system and to stabilize the active MoS during the reaction; it has been used in a similar way for HDO [33] and hydrodesulfurization [34]. Note that the absence of DMDS during hydrocracking led to the significant formation of cokes, indicating poor hydrocracking activity. The agitation rate was increased to 300 rpm when the reaction temperature was reached. Hydrocracking was isothermally performed at the desired reaction temperature for 60–240 min, after which the reactor was cooled to 30 °C and depressurized to ambient pressure. The mixture of liquid products and catalyst was centrifuged at 3000 rpm for 3 min to separate the liquid products from the cokes and solid catalyst powder. The liquid products, hydrocracked (HCK) oils, were weighed, and their yields were determined using the expression (hydrocracked oil yield, %) = (weight of hydrocracked oil)/(weight of lignin pyrolysis oil reactant) \times 100, after which they were further characterized by GC/MS, GPC, Karl-Fischer analysis, elemental analysis, and viscometry. The solid fractions were dried and subjected to TG analysis to quantify the coke formation; the coke yield was calculated as (coke yield, %) = (weight of coke)/(weight of lignin pyrolysis oil reactant) \times 100.

Next, the recyclability of CoMo/H β was then tested. For each run of the recycling test, 0.5 g of CoMo/H β was mixed with 5 g of lignin pyrolysis oil and 0.05 g of DMDS. Room-temperature H_2 gas was added to the reaction mixture at a pressure of 100 bar, and the reaction was performed at 400 °C for 60 min. After each run, the spent catalyst powder was washed with ethanol and calcined using 1% (v/v) O_2/N_2 at 350 °C for 1 h prior to the next run.

2.5. Hydrodeoxygenation

Lignin pyrolysis oil dissolved in the HCK oil was hydrodeoxygenated in a continuous-flow fixed-bed reactor with a length of 500 mm and an internal diameter of 1.27 cm (Fig. 2). The catalyst (10 g, 5 wt% Ru/TiO $_2$) was loaded into the reactor and reduced under ambient pressure at 350 °C for 3 h under flowing H_2 (200 mL/min). The reactor was then

Table 1
Characterization results for the lignin pyrolysis oil reactant.

Property	
C (wt%)	70.80
H (wt%)	7.13
N (wt%)	1.48
S (wt%)	0.66
O (wt%)	20.99
O/C (mol/mol)	0.22
H/C (mol/mol)	1.2
Viscosity at 25 °C (cP)	751
Moisture (wt%)	2.0
HHV (MJ/Kg)	30.4

pressurized to 100 bar at 350 °C, under the control of a back pressure regulator. The flow of H_2 was increased to 600 mL/min, and the lignin pyrolysis oil dissolved in the HCK oil was fed into the reactor with the temperature of reactor being maintained at 350 °C during the HDO reaction. The flow rate of the liquid reactant mixture was 2–2.5 g/h, and the weight hour space velocity (WHSV) was 0.2–0.25 h $^{-1}$. The liquid products were weighed, and their yields were determined using the expression (hydrodeoxygenated oil yield, %) = (weight of produced oil)/(weight of reactant oil) \times 100, after which they were further characterized by GC/MS, viscometry, and elemental analysis.

3. Results and discussion

3.1. Characterization of the lignin pyrolysis oil reactant

Prior to hydrocracking and hydrodeoxygenating the lignin pyrolysis oil prepared by pyrolyzing the Kraft lignin, its high viscosity and oxygen content were measured (Table 1). As a superficially homogeneous complex mixture, the lignin pyrolysis oil was highly viscous and sticky, with a measured viscosity of 751 cP. Such viscosity precludes its use in a continuous-flow reaction without being dissolved in a solvent because the reactor may become plugged by the highly viscous lignin pyrolysis oil. GC/MS of the lignin pyrolysis oil revealed the presence of phenolic and aromatic monomers (retention times: 10–35 min) along with complex polycyclic compounds (retention times: 35–50 min) (Fig. 3). In addition to these distillable products, more-complex higher-carbon-number hydrocarbons, oligomers, and polymers may also have been present in the lignin pyrolysis oil. Many of these oligomers and polymers could not be evaporated or detected by GC/MS but may have contributed to the high viscosity of the oil. Most compounds detected by GC/MS were oxygenates, including phenolic compounds, which must have formed from phenolic lignin monomers (*p*-coumaryl, coniferyl, and sinapyl alcohols) [35]. A large amount of oxygen (20.99 wt%), but a small quantity of moisture (2.0 wt%), was determined, indicating that most of the oxygen atoms exist as organic oxygenates, including phenolic compounds, rather than as water.

3.2. Hydrocracking of lignin pyrolysis oil

Because the high viscosity of the lignin pyrolysis oil precludes the use of continuous-flow reactions, lignin pyrolysis oil was hydrocracked to produce less-viscous oil by cracking oligomers and polymers into smaller molecules. Batch reactions in the presence of DMDS at 400 °C for 120 min using CoMo/Al $_2$ O $_3$ or CoMo/H β as the catalyst significantly reduced the viscosity to 13 or 7.6 cP, respectively (Table 2). In addition, the O/C atomic ratio significantly decreased, from 0.22 (lignin pyrolysis oil) to 0.060–0.082, indicating that ether and hydroxyl bonds were hydrocracked to form deoxygenated compounds.

The results obtained using CoMo/Al $_2$ O $_3$ and CoMo/H β as catalysts indicated that CoMo/H β provided a higher yield of liquid products (70.5%) and less coke (1.6%). GC/MS revealed the loss of compounds

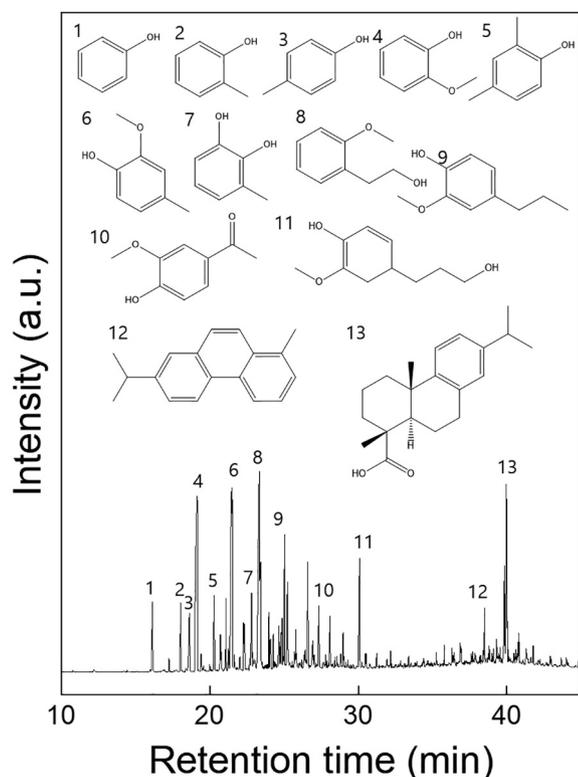


Fig. 3. GC/MS results for the lignin pyrolysis oil reactant.

with higher carbon numbers from the lignin pyrolysis oil and that smaller molecules were produced in the HCK oils (Figs. 4(a) and S2(a)). Higher-carbon-number compounds were eliminated and large amounts of smaller molecules were more significantly formed over CoMo/Al₂O₃, indicative of better hydrocracking performance. Considerable amounts of deoxygenated aromatic compounds and cycloalkanes were observed to form over CoMo/Al₂O₃, while only small amounts formed over CoMo/H β , confirming the superior hydrocracking and HDO activity of CoMo/Al₂O₃. Although the formation of deoxygenated compounds is desirable for upgrading biomass pyrolysis oils, the loss of liquid

products caused by cracking the lignin pyrolysis oil and the formation of cokes during the deep deoxygenation to provide the deoxygenated hydrocarbons must both be minimized. Based on these observations, CoMo/H β , which produces a higher yield of liquid products and a lower yield of coke, was selected as the optimum catalyst.

GPC also revealed that both the catalysts formed smaller molecules (higher retention times) and eliminated larger molecules (lower retention times) (Figs. 5(a), S3(a), and Table 2). When calibrated against the GPC polystyrene standard, the M_w of the lignin pyrolysis oil was determined to be 286 g/mol, which was reduced to 215 and 178 g/mol following reaction over CoMo/Al₂O₃ and CoMo/H β , respectively, confirming that the heavy molecules in the lignin pyrolysis oil were hydrocracked.

CoMo/Al₂O₃ and CoMo/H β were characterized using ICP-OES, TEM, XRD, and N₂ physisorption. The ICP-OES results indicated that their Co and Mo contents were almost the same: 3.0 wt% Co/7.4 wt% Mo and 3.1 wt% Co/8.7 wt% Mo were obtained for CoMo/Al₂O₃ and CoMo/H β , respectively (Table S3). EDS mapping with the TEM confirmed the presence of Co and Mo species in both catalysts (Fig. S4). However, the XRD results did not reflect the presence of Co and Mo because of their low concentrations in the catalysts, but distinct diffraction peaks of crystalline zeolite β (for CoMo/H β) and γ -Al₂O₃ (for CoMo/Al₂O₃) were observed (Fig. S5). N₂ physisorption indicated that CoMo/H β had a much higher BET surface area because of the large micropores of H β . However, CoMo/Al₂O₃ had a larger external surface area of CoMo/Al₂O₃, which is accessible by the high-molecular-weight reactants (Table S3 and Fig. S6).

3.3. Effects of reaction temperature on hydrocracking

CoMo/H β was selected for further study based on the results obtained at 400 °C for 120 min, as discussed in Section 3.2, but the effects of reaction temperature were further investigated (Table 2, Figs. 4(b), and S2(b)). Catechols (i.e., catechol and its alkyl-branched derivatives) and coniferyl alcohols were observed when the reaction was performed at low temperatures (300 °C) for 60 min, indicating that phenolic monomers were incompletely cracked (Figs. 4(b) and S2(b)). The amounts of these phenolic compounds, which were probably derived from the coniferyl and sinapyl alcohols of lignin monomers, decreased with the increasing reaction temperature. Although the cracking of complex monomers increased with increasing reaction temperature, the

Table 2
Hydrocracking results for the lignin pyrolysis oil.^a

Catalyst	Reaction conditions		Yields				Viscosity of hydrocracked oil (cP)	Elemental compositions of liquid products		GPC results		
	Reaction temperature (°C)	Reaction time (min)	Hydrocracked oil yield (wt%)	Coke yield (wt%)	Moisture in hydrocracked oil (wt%)	Mass balance (wt%) ^b		O/C (mol/mol)	H/C (mol/mol)	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)
(Lignin pyrolysis oil)					2.0		751	0.22	1.2	286	164	1.7
CoMo/Al ₂ O ₃	300	120	94.7	2.2	6.8	96.9	206	0.16	1.3	585	266	2.2
CoMo/Al ₂ O ₃	350	120	79.3	1.4	5.1	80.7	47	0.11	1.3	385	202	1.9
CoMo/Al ₂ O ₃	400	120	62.2	5.0	2.7	67.2	13	0.060	1.2	215	100	2.2
CoMo/H β	300	60	89.0	1.4	4.6	90.4	205	0.13	1.3	519	241	2.3
CoMo/H β	350	60	78.5	3.6	4.4	82.1	189	0.11	1.2	485	211	2.3
CoMo/H β	400	60	76.6	1.6	3.4	78.2	21	0.11	1.3	271	147	1.8
CoMo/H β	300	120	86.6	2.0	5.0	88.6	276	0.16	1.5	429	211	2.0
CoMo/H β	350	120	76.8	1.8	5.0	78.6	42	0.081	1.3	362	159	2.3
CoMo/H β	400	120	70.5	1.6	4.3	72.1	7.6	0.082	1.3	178	107	1.7
CoMo/H β	300	240	79.9	1.6	4.10	81.5	207	0.11	1.3	433	218	3.0
CoMo/H β	350	240	75.8	3.4	20.9	79.2	178	0.096	1.2	450	189	2.4
CoMo/H β	400	240	72.3	1.2	3.5	73.5	3.2	0.080	1.3	168	93	1.8

^a Reactant: lignin pyrolysis oil (5 g), pressure: 100 bar H₂, catalyst: 0.5 g, DMDS: 0.05 g, agitation rate: 300 rpm.

^b Sum of the yields of coke and hydrocracked oil. The loss can be attributed to gaseous and evaporated volatile products, as depicted in Fig. S1.

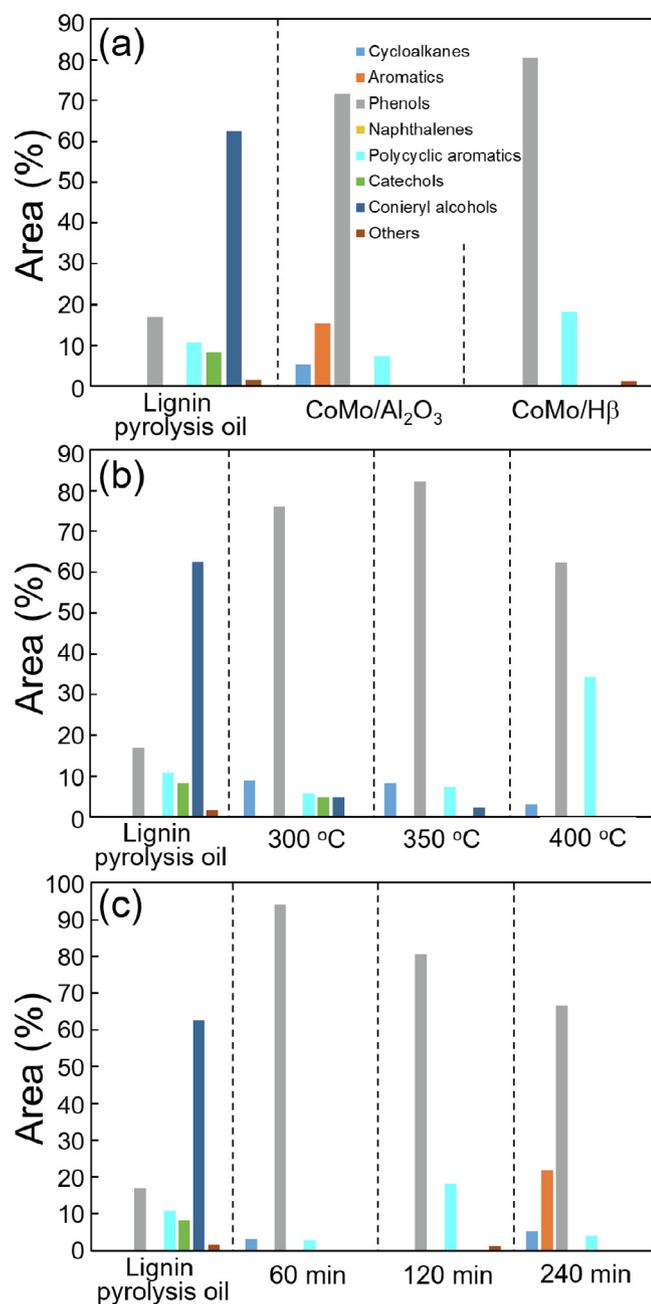


Fig. 4. GC/MS-based compositions of the hydrocracked lignin pyrolysis oil depending on (a) catalyst (at 400 °C for 120 min), (b) reaction temperature (using CoMo/H β for 60 min), and (c) reaction time (using CoMo/H β at 400 °C). H₂ pressure was 100 bar at room temperature in all cases.

liquid-product yield decreased from 89.0 to 76.6% as the reaction temperature was increased from 300 to 400 °C. The molecular weight and viscosity were also observed to decrease with the increasing reaction temperature, suggesting that hydrocracking was more effective at the higher reaction temperature (Table 2, Figs. 5(b), and S3(b)).

The GPC results (Fig. 5(b)) demonstrated that after reacting at 300–350 °C, the quantity of large molecules (detected at low retention times) exceeded that of the lignin pyrolysis oil, suggesting possible repolymerization at lower temperature (Fig. S3(b)). However, the higher number of large molecules appears to contradict the lower observed viscosity. Although the viscosity of a polymer strongly depends on its molecular weight, in our case, higher-molecular-weight polymers exhibit lower viscosities because the chemical functionalities of the lignin pyrolysis oil become significantly degraded during

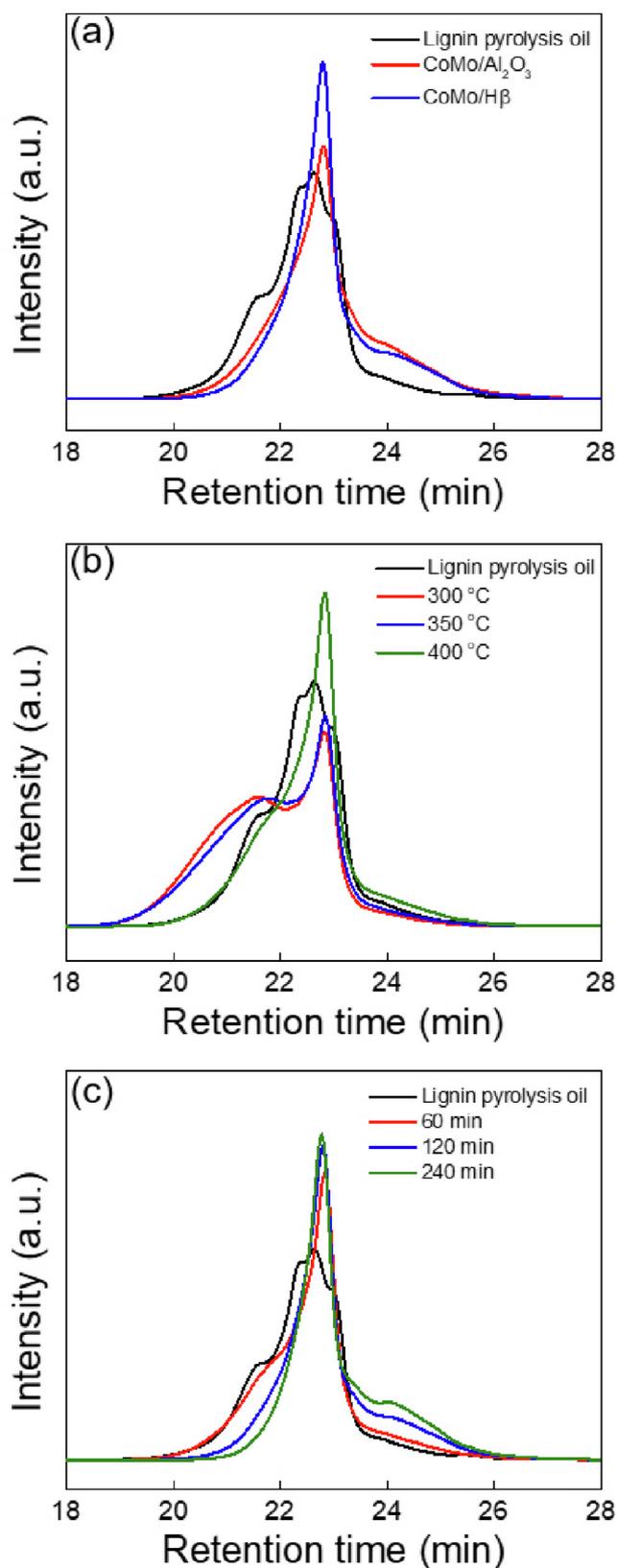


Fig. 5. GPC results for the hydrocracked oils depending on (a) catalyst (at 400 °C for 120 min), (b) reaction temperature (using CoMo/H β for 60 min), and (c) reaction time (using CoMo/H β at 400 °C). H₂ pressure was 100 bar at room temperature in all cases.

hydrocracking. Based on the molecular weight and viscosity, we conclude that a reaction temperature of 400 °C can most efficiently hydrocrack lignin pyrolysis oil.

3.4. Effects of reaction time on hydrocracking

Because repolymerization to form larger molecules was observed at lower temperatures, the reaction-time-dependent hydrocracking behavior was further studied (Table 2, Figs. 4(c), and S2(c)). At a fixed reaction temperature of 350 °C, the liquid yield decreased slightly, from 78.5 to 75.8%, as the reaction time was increased from 60 to 240 min. The GC/MS results indicated that aromatic and polycyclic aromatic compounds increasingly formed with increasing reaction time, consistent with the repolymerization of hydrocracked oil suggested above (Fig. 4(c)). The GPC results also exhibited the increased formation of both large and small molecules, with higher peak intensities at both shorter and longer retention times (Fig. 5(c)). Although improved cracking and repolymerization were observed, the average molecular weight was lower, which indicated more significant cracking to form small molecules (Table 2 and Fig. S3(c)).

3.5. Catalyst recyclability

The recyclability of CoMo/H β was determined by re-using the spent CoMo/H β in repeated batch reactions. Each run was performed at 400 °C for 60 min with H₂ at 100 bar (measured at room temperature) (Table 3). The spent catalyst powder was regenerated by washing with ethanol and calcination using 1% (v/v) O₂/N₂ at 350 °C for 1 h. The hydrocracking activity of the spent CoMo/H β was maintained up to the fourth run, with a produced HCK oil viscosity of 15.9–20.9 cP.

3.6. Reaction pathway and gas-phase products

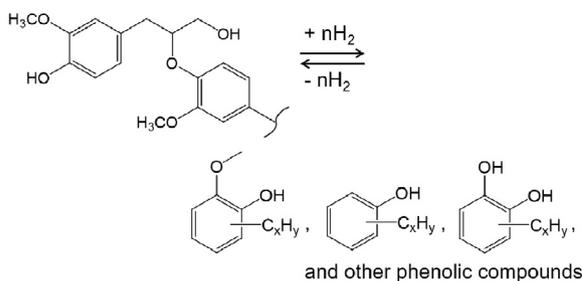
GC/MS revealed that the gas-phase products formed over both CoMo/H β and CoMo/Al₂O₃ include light hydrocarbons, viz. ethane, 2-methylpropane, n-butane, 2-methylbutane, n-propane, and methylcyclopentane, as well as deoxygenated aromatic compounds, including benzene, methylcyclohexane, and toluene (Fig. S1). These light hydrocarbons are produced by the dealkylation of lignin pyrolysis oil products during hydrocracking. Because the phenols (i.e., phenol and phenol derivatives with alkyl groups) and coniferyl alcohols in the lignin pyrolysis oil contained methyl, ethyl, and propyl substituents, the fragments formed by their dealkylation further condensed with other fragments and isomerized to iso-alkanes. Notably, although methane was not observed in this study, it theoretically could have been formed by hydrogenation following the fragmentation of the methoxy groups of the coniferyl alcohols; thus, its possible formation cannot be excluded. The aromatic compounds observed in the gas-phase products were molecules that had vaporized during hydrocracking and were generated when oxygen functionalities were removed from the phenols and coniferyl alcohols in the lignin pyrolysis oil. Based on these observations, along with the liquid-product characterization results, we have proposed several reactions that occur during hydrocracking (Fig. 6). During hydrocracking, the hydroxyl and alkoxy functional groups of

Table 3
Recyclability test of CoMo/H β for hydrocracking.^a

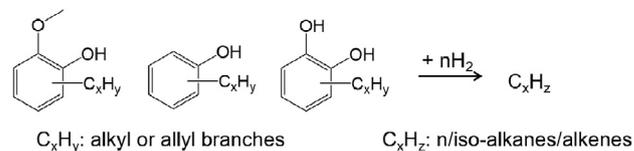
Run	Hydrocracked oil yield (wt %)	Coke yield (wt %)	Moisture in hydrocracked oil (wt%)	O/C (mol/mol)	H/C (mol/mol)	Viscosity of hydrocracked oil (cP)	M _w (g/mol)	M _n (g/mol)
1	76.6	1.6	3.42	0.11	1.3	20.9	271	147
2	71.4	1.8	3.56	0.10	1.3	20.0	250	130
3	76.4	1.4	4.55	0.14	1.3	16.1	281	158
4	73.2	1.8	4.73	0.12	1.3	15.9	235	119

^a Reaction conditions for each run: 0.5 g of CoMo/H β , 5 g of lignin pyrolysis oil, 0.05 g of DMDS, 100 bar H₂ at room temperature, reaction temperature = 400 °C, reaction time = 60 min. The spent catalyst powder was washed with ethanol and calcined using 1% (v/v) O₂/N₂ at 350 °C for 1 h.

Hydrocracking & repolymerization:



Dealkylation & isomerization:



Hydrodeoxygenation:

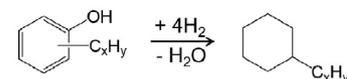


Fig. 6. Proposed reaction pathway for hydrocracking lignin pyrolysis oil.

the phenols and coniferyl alcohols in the lignin pyrolysis oil are removed to produce phenols and deoxygenated aromatic compounds. As observed in our previous studies on phenolic model compounds [36,37], cracking and condensation occur over the solid acid catalysts. The hydrogenolysis of ether bonds can crack the high molecular weight lignin molecules to form smaller ones. The ethers can be isomerized or condensed via C–C bond formation, which may be involved in repolymerization, and the dealkylation of alkyl phenols during lignin depolymerization [11,12] can produce phenols and aliphatic compounds including paraffins and olefins. Finally, the produced phenols and alkyl phenols can be hydrodeoxygenated to alkyl cyclohexanes.

The calculated mass balances, which are the sums of the coke and HCK oil yields, indicated that smaller quantities of coke and HCK oil were collected when a lower viscosity was achieved by hydrocracking (Table 2). These observations confirmed that the formation of less-viscous HCK oil can accompany the formation of smaller cracked molecules by hydrocracking, with concomitant reduction in HCK oil yield.

3.7. Rheological properties of the hydrocracked oil

The rheological properties of the HCK oil were further examined because viscous liquids are difficult to transport. The viscosity was observed to increase with increasing molecular weight (Fig. 7), following the relationship: viscosity $\propto M_w^{3.54}$, which is close to the relationship reported for entangled linear polymers (viscosity $\propto M_w^{3.4}$) [38]. The viscosity and shear rate were also correlated (Fig. S7). Two

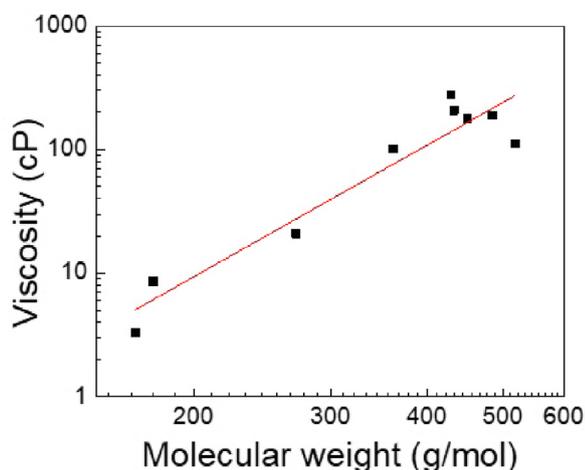


Fig. 7. Viscosity dependence on molecular weight. (Regression line: (Viscosity, cP) = $6.58 \times 10^{-8} \times (\text{Molecular weight, } M_w, \text{ g/mol})^{3.54}$)

HCK oils with significantly different viscosities of 170 (hydrocracked at 350 °C) and 5 cP (hydrocracked at 400 °C) were used to correlate the viscosity and shear rate, and viscosity was observed to remain constant as a function of shear rate, indicating that these HCK oils are Newtonian fluids, which are appropriate for high-pressure reactions.

3.8. Dissolving the lignin pyrolysis oil in the hydrocracked oil as a solvent

Because of its significantly reduced viscosity, the incompletely deoxygenated HCK oil was used as a solvent for the lignin pyrolysis oil (Table S2, Figs. 8, and S8). Adding the HCK oil, which was prepared using CoMo/H β at 400 °C for 120 min, to the lignin pyrolysis oil significantly decreased its viscosity, namely, from 751 cP to 210 cP upon addition of 10 wt% of the HCK oil. In contrast to the HCK oil, hydrodeoxygenated compounds with negligible oxygen functionalities [13,14] did not dissolve the lignin pyrolysis oil. The higher solubility of the lignin pyrolysis oil in the HCK oil is attributable to the lignin moieties that remain following hydrocracking, as these moieties improve the interactions between the polar oxygenated molecules in the lignin pyrolysis oil and the HCK oils, whereas nonpolar molecules in the hydrodeoxygenated products are phase-separated with the polar molecules in the lignin pyrolysis oil (Fig. S8). Because HDO is highly exothermic, its reaction temperature is difficult to control, which has hindered the scale-up of the HDO process. While using liquid products as recycled solvents during the practical operation of chemical processes has been explored, the HDO product cannot be used as a solvent because it cannot dissolve biomass-derived pyrolysis oil. Therefore, employing HCK oil is a feasible strategy for reducing the heat released during the HDO process, and it also offers better scale-up opportunities.

3.9. Hydrodeoxygenation of the lignin pyrolysis oil dissolved in a hydrocracked oil

Lignin pyrolysis oil (70 wt%) was dissolved in the prepared HCK oil and further hydrodeoxygenated in a continuous-flow reactor (Table 4 and Fig. S9). As depicted in Fig. 8 and summarized in Table S2, the sticky lignin pyrolysis oil became less viscous, and the lignin pyrolysis oil diluted with the HCK oil did not clog the continuous-flow fixed-bed HDO reactor. GC/MS revealed the formation of deoxygenated compounds, including cyclohexane and alkylcyclohexanes in the HDO products, unlike the composition of the reactant. Specifically, the lignin pyrolysis oil dissolved in HCK oil is composed of phenol and alkylphenols. These observations confirm that benzene rings become saturated and that hydroxyl groups are removed from alkylcyclohexanols during HDO [25]. Successful deoxygenation was also observed,

confirming that oxygen functionalities are removed to form deoxygenated hydrocarbons. The O/C ratio decreased from 0.19 (mol/mol) (70 wt% lignin pyrolysis oil dissolved in the HCK oil) to 0.027 (mol/mol), which represents an 86% decrease based on the reactant mixture and an 88% decrease based on the raw lignin pyrolysis oil. Deoxygenated products, including cyclohexane, alkylcyclohexanes, and dimeric cyclohexanes, were also confirmed using GC/MS (Fig. S9). Note that the HDO of HCK oil also produced deoxygenated products with properties that were almost identical to those prepared by the HDO of 70 wt% lignin pyrolysis oil dissolved in the HCK oil (Table 4 and Fig. S9).

Based on these observations, we propose the continuous-flow HDO of lignin pyrolysis oil dissolved in a HCK oil (Fig. 9). While directly applying this process to raw lignin pyrolysis oil is impossible because of its high viscosity, a mixture of lignin pyrolysis oil dissolved in its HCK oil, which has a significantly lower viscosity than the raw lignin pyrolysis oil, can be transported to the hydrocracking reactor. The hydrocracked mixture is split into two streams; one can be recycled for mixing with raw lignin pyrolysis oil, and the other can be further transported to the second reactor for HDO to produce deoxygenated hydrocarbon fuels. In this way, a multi-step continuous flow reaction can be achieved, along with the continuous production of deoxygenated fuels from lignin pyrolysis oil.

4. Conclusion

The hydrocracking of lignin pyrolysis oil significantly reduced its viscosity. Coniferyl alcohols, phenolic oligomers, and complex phenols were converted into less-complex compounds, including phenols and deoxygenated aromatic molecules, as determined by GPC and GC/MS, which decreased the product viscosity. Although hydrocracking reduced viscosity under all the reaction conditions used in this study, the lower-temperature reaction (≤ 350 °C) increased both repolymerization (to larger molecules) and cracking (to smaller molecules), while the higher temperature reaction (400 °C) did not increase repolymerization. Because of the chemical similarities between the raw lignin pyrolysis oil and the HCK oil compared to the fully deoxygenated liquid, the lignin pyrolysis oil was found to be highly soluble in the hydrocracked oil. The homogenous lignin-pyrolysis-oil/hydrocracked-oil mixture was hydrodeoxygenated in a continuous-flow reactor, whereas continuous-flow reactors cannot be operated using the pure lignin pyrolysis oil because of its high viscosity. The HCK oil can be used to dissolve lignin pyrolysis oil, which may lead to the development of continuous-flow HDO processes with recycling units for HCK oil; this is a useful breakthrough for the commercialization of the biomass pyrolysis-oil upgrading process.

The main advances of this study over previous attempts to use lignin pyrolysis to produce fuel are the following: (i) Continuous flow reaction using lignin-derived reagents, including raw lignin pyrolysis oil and its HCK oil, has been achieved. Although the raw lignin pyrolysis oil is too viscous for a continuous-flow reaction, an effective and feasible strategy for continuously upgrading lignin pyrolysis oil without n-butanol or THF solvent has been developed. (ii) Kraft lignin has been used, which is a mass-produced waste product in the pulping industry and is much cheaper than organosolv or milled-wood lignins. Employing this waste to produce fuel is a useful strategy for detoxifying and valorizing environmentally poor resources. (iii) Using a bio-refinery to valorize sugars from lignocellulose produces significantly large amounts of lignin waste, but valorizing this lignin has been a challenge. Pyrolysis followed by upgrading for fuel production is a simple method for valorizing diverse lignin resources. Therefore, producing fuels from lignin pyrolysis oil represents a potentially useful process for valorization of lignin waste, although significant efforts will be required to develop an industrially feasible process.

Table 4
HDO results using the HCK oil as the solvent.

Liquid product	Viscosity (cP)	Liquid yield (%)	C (wt%)	H (wt%)	O (wt%)	S (wt%)	N (wt%)	O/C (mol/mol)	H/C (mol/mol)	HHV (MJ/Kg)
Lignin pyrolysis oil	751	–	70.8	7.13	21.0	0.66	1.48	0.22	1.2	30.4
HCK oil ^a	20	–	77.6	8.34	11.3	0.0	1.17	0.11	1.3	36.1
HDO product of HCK oil ^b	< 1	35.9	85.0	13.4	3.07	0.0	1.32	0.027	1.9	47.4
70 wt% lignin pyrolysis oil dissolved in HCK oil ^a	111	–	72.8	7.49	18.1	0.46	1.39	0.19	1.2	32.2
HDO product of lignin pyrolysis oil dissolved in HCK oil ^b	< 1	43.3	87.2	13.7	3.16	0.0	1.20	0.027	1.9	48.6

^a HCK oil was prepared by hydrocracking the lignin pyrolysis oil at 400 °C with 100 bar H₂ (measured at room temperature) for 1 h using CoMo/H β as the catalyst.

^b Catalyst: 5 wt% Ru/TiO₂, reaction temperature: 350 °C, pressure: 100 bar H₂, WHSV = 0.2–0.25 h⁻¹,

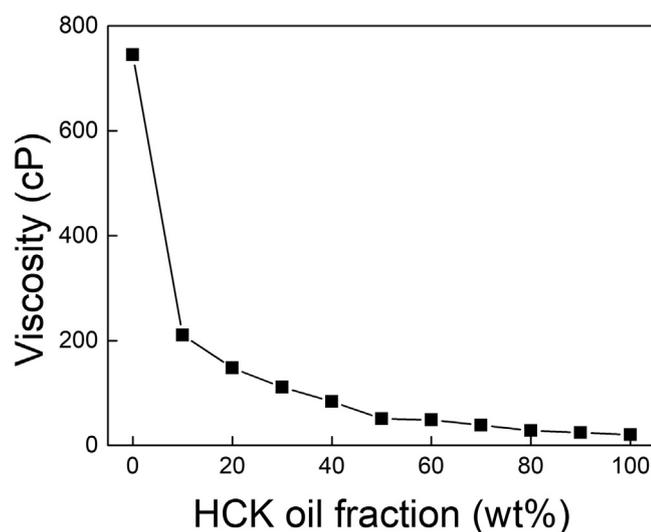


Fig. 8. Viscosities of mixtures of lignin pyrolysis oil and HCK oil.

CRediT authorship contribution statement

Yoonsoo Kim: Investigation, Writing - original draft. **Jingi Shim:** Investigation. **Jae-Wook Choi:** Methodology, Investigation. **Dong Jin Suh:** Conceptualization, Funding acquisition. **Young-Kwon Park:** Methodology, Investigation. **Ung Lee:** Data curation. **Jungkyu Choi:** Supervision. **Jeong-Myeong Ha:** Conceptualization, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.enconman.2020.112728>.

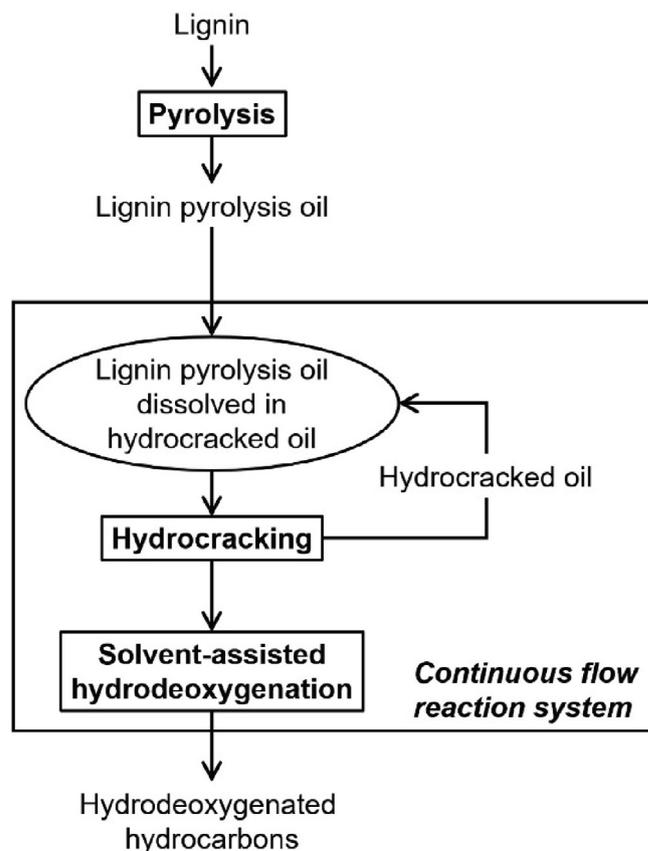


Fig. 9. Suggested continuous-flow HDO of lignin pyrolysis oil dissolved in its HCK oil.

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