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Hydrocracking of Biomass-Derived Materials into Alkanes in the Presence of Platinum-Based Catalyst and Hydrogen

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Abstract Renewable green C2–C9 alkanes can be directly produced by Pt/H-ZSM-5-catalyzed hydrocracking of biomass-derived materials, no pre-treated or pre-treated by alcohol. The pre-treatment of cellulose in 1-hexanol at 623 K, followed by hydrocracking catalyzed by Pt/H-ZSM-5(23) at 673 K, produced C2–C9 alkanes in as high as 89% yields with CH_4/CO_x yields of only 6%. The reaction pathway involves lowering of molecular weight of cellulose materials, producing, probably, oxygenates intermediates such as mono-saccharide and disaccharide, which are further efficiently converted to alkane products by successive hydrocracking and condensation, catalyzed by Pt/H-ZSM-5.

Keywords Pt/H-ZSM-5 · Hydrocracking · Alcohol pre-treatment · C2–C9 alkanes

1 Introduction

Due to the advantages of being CO_2 neutral, having low sulfur content, and being easy to transport, renewable biomass resources will become more important in the future as alternatives to fossil fuels. In addition, 240 million tons of biomass wastes such as the lignocellulosics are generated annually in Japan, of which 65 million tons are not used effectively [1]. Therefore, technology that can convert them to valuable liquid fuels and chemicals will be important for solving our energy and environmental problems. In general, gasification and fermentation are used for biomass conversion. Gasification needs very high temperature of 900–1,000 °C and subsequent liquefaction processes of biogas such as Fischer–Tropsch reaction and methanol synthesis are required for obtaining liquid fuel. Fermentation proceeds at mild conditions, but slow productivity, pretreatment of biomass and fermentation wastes are still problem to be solved.

Pyrolysis is one of a thermochemical process that is an efficient way of converting biomass into gases, liquids, and char at temperature as relatively low as 573–873 K. Of these products, we are interested in liquids for fuels as well as chemicals. To our knowledge, most pyrolysis process is performed under inert gas conditions. But in these cases, pyrolysis reactor design, reaction parameters (temperature, heating rate, residence time, pressure, and catalyst), and biomass type and characteristics (particle size, shape, and structure) have strong effects on the yield and properties of the products formed [2]. Also, since obtained liquids contain 40–45 wt% of oxygen as organic compounds such as phenol derivatives, additional hydrotreating process is required for deoxygenation.

Fluid catalytic cracking (FCC) is the most widely used process for the conversion of vacuum gas oil (VGO) [3]. In this process, no additional hydrogen is required and aromatics are major products. The conversion of carbohydrates and lignin over H-ZSM-5 catalysts has been reported and major products are coke, CO, aromatics, and CO2 [4, 5]. Hydrotreating of bio-oil and lignin using Co–Mo and Ni–Mo catalysts produced C7–C11 alkylbenzenes C5–C11 branched alkanes, but hydrocracking of cellulose and wood has not been reported [6, 7].

Hence, in this work, an attempt was made to investigate the effect of hydrogen on the pyrolysis product yield, in which liquid and, partly, gaseous alkanes are expected to

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be major products. As biomass materials, cellulose and wood flour are used. The present study also included comparison of yields of C2–C9 alkanes with and without alcohol pretreatment, prior to hydrocracking.

2 Experimental

Cellulose and organosolv lignin were obtained from Aldrich Chemicals. Wood tip samples such as eucalyptus, cedar, and Douglas fir used in this study were given from Oji paper Co. Ltd. Pyroligneous acid (Wood vinegar) was purchased from Kishu-Sin-Binchotan Co. The wood vinegar contains AcOH, ethylene glycol, glycerol, methanol and acetone, as ascertained by GC-FID analysis. Elemental analysis of the vinegar shows 4.31 wt% of carbon and 10.2 wt% of hydrogen. The wood vinegar was used without any pretreatment. Elemental analysis of organosolv lignin was C (44.12%), H (45.90%), and O (9.98%) [8]. These wood tips were sieved to obtain the average particle size of ca. 1 mm. Microporous materials such as H-ZSM-5 and USY were provided by Zeolyst and Tosoh Co. Ltds. The Si/Al ration of these zeolites were given in the table and also, the Si/Al ratio of silica–alumina was 2.2. $Pt(NH_3)_4Cl_2{\cdot}H_2O$ and NH_4ReO_4 were purchased from Soekawa Chemicals, Japan. The Pt/zeolite catalyst used in this study was prepared by impregnating zeolite support with $Pt(NH_3)_4Cl_2{\cdot}H_2O$, followed by drying at 373 K and calcination for 5 h at 773 K. Pt–Re/zeolite was prepared by impregnation of zeolite with $Pt(NH_3)_4Cl_2{\cdot}H_2O$ followed by drying at 373 K and calcination for 5 h at 773 K. The concentrations of platinum metal were 1 wt% [9].

Hydrocracking experiments were carried out using a 100-cm^3 autoclave-type reactor. In a one-pot reaction, the catalyst (1.0 g) was introduced into the autoclave and pretreated by reduction with 2 MPa of H_2 at 473 K for 5 h. After the reduction, 1 g of cellulose (or wood vinegar) was introduced with 9 g of H_2O and the autoclave was pressurized with 6.5 MPa of H_2/N_2 gas mixture (H_2/N_2 = 91/9 vol.%). The reaction was carried out at 573–673 K for 12 h with vigorous stirring by using shaking-type furnace. In a two-step reaction, cellulose or wood flour (1 g) and solvent (10 mL) such as 1-hexanol were introduced into the autoclave and pretreated with 2 MPa of Ar at 623 K for 2 h. After cooling down, gas was removed. Then, the solvent was roughly distilled away in vacuo and the obtained slurry-like product was immediately returned to the autoclave with pre-reduced catalyst (1 g) and H_2O (9 g), followed by re-pressurization with 6.5 MPa of H_2/N_2 gas mixture. The reaction was performed at 673 K and 12 h.

After one- or two-step reaction, the gaseous and liquid products were collected and analyzed by off-line FID and TCD gas chromatographies. For gaseous products, Porapak Q column for FID and Porapak Q and MS 5A columns for the TCD were used. Liquid products were extracted with 10 mL of tetradecane (C14) and organic phase was analysed by FID GC, where SE-30 column was used. TCD analysis was performed using N_2 internal standard, while, for FID analysis, hexacosane (C26) was used as internal standard. The each carbon selectivity is defined as the moles of carbon in each product divided by the total carbon in the feed. The amount of total carbon soluble in water liquid phase was estimated by elemental analysis and the amount of carbon deposit over the catalyst surface was analysed by thermo-gravimetric analysis under air conditions.

3 Results and Discussion

The hydrocracking reactions of wood vinegar were carried out at 573 K for 12 h.

Table 1 summarizes a detail of hydrocarbons and CO and CO_2 products (Abbreviated as CO_x). At 603 K over Pt/H-ZSM-5(23), 100% yield was achieved from organic oxygenates contained in wood vinegar and ca. 50% of C1 and C2 alkanes were formed, probably from C1/C2 oxygenates such as methanol and AcOH. As other products, C3–C4, C5+ and CO_x were detected, in which C5+ would be formed by condensation of carbon species. Lower conversions and (C1 + C2) selectivities were obtained over USY(6.3) and SiO2-Al2O3 than those of H-ZSM-5(23), indicating less sufficient hydrocracking ability than that of H-ZSM-5 support. Thus, in the presence of Pt/H-ZSM-5 catalyst, lower hydrocarbons were mainly formed by hydrocracking of wood vinegar.

Next, a direct hydrocracking of cellulose was examined. The yield into (alkanes + CO_x) was 42.1%, which is sum of gaseous and liquid products. The selectivity to C2–C9 hydrocarbons was 29.7%, while CO_x selectivity was 40.9% with 18.9% of C10+ alkanes and 10.6% of CH_4, as shown in Table 2.

In the presence of catalyst, both the yield and selectivity into alkanes were increased and CO_x selectivity decreased. For Pt/USY(6.3), the conversion was 97.2% and C2–C9 selectivity was 38.4% with 18.5% of C10+ selectivity and 31% of CO_x with 12% of CH_4. The amount of carbon deposited on catalyst surface was 2.8%, ascertained by thermo-gravimetric analysis. So, the carbon balance was approximately 100%. When Pt/H-ZSM-5 catalysts were used, C2–C9 selectivities were close to that of Pt/USY(6.3), while CH_4 selectivities were higher and CO_x selectivities were lower than that of Pt/USY(6.3). Also, total alkane selectivities were 77.9% for Pt/H-ZSM-5(23) and 88.6% for Pt/H-ZSM-5(30), while the cellulose conversions were decreased to 89.1 and 69.7%. Then, the reaction was carried

Table 1 Hydrocracking of wood vinegar

Support[a]	Yield into (alkanes + CO_x) (%)[c]	Carbon selectivity (%)				
		CH_4 (%)	C2 (%)	C3–C4 (%)	Residue[d] (%)	CO_x (%)
H-ZSM-5	74.7	21.8	25.3	8.66	23.2	21.0
H-ZSM-5[b]	100	22.5	28.4	14.6	10.3	24.3
USY	48.1	5.27	14.5	13.4	56.0	10.7
SiO_2–Al_2O_3	17.9	4.55	0	29.8	65.6	0

Conditions: 1 wt% Pt/support, 1.0 g; wood vinegar, 9 mL; T = 573 K; 12 h; P = 6.5 MPa; $H_2/N_2 = 9/1$. Pretreatment at 473 K and 2 MPa of H_2 for 4 h

[a] H-ZSM-5 (23) and USY (6.3) were used

[b] 603 K

[c] Yield = (sum of C-containing products)/carbon initially added * 100

[d] Residue selectivity = 100 − sum of ((C1 − C4) and CO_x selectivities)

Table 2 Hydrocracking of cellulose under hydrogen conditions

Catalyst	Temp. (K)	Yield into (alkanes + CO_x) (%)[f]	Carbon selectivity (%)[g]						
			CH_4	C2–C4	C5–C9	C10–C20	C21+	Oxy[h]	CO_x
None	673	42.1	10.6	18.9	10.8	16.4	2.47	0	40.9
Pt[a]/H-ZSM-5 (23)[c]	673	89.1	17.6	21.8	17.5	18.7	2.22	0.00	22.1
Pt[a]/H-ZSM-5 (30)[c]	673	69.7	28.7	19.0	18.6	21.0	1.21	0	11.4
Pt[a]/USY (6.3)[c]	673	97.2	12.0	20.6	17.8	14.5	3.96	0	31.0
PtRe[b]/H-ZSM-5 (23)[c]	573[d]	51.8	14.5	18.6	58.2	1.09	1.76	0.04	0
PtRe[b]/H-ZSM-5 (23)[c]	543[e]	64.7	3.67	34.9	40.9	7.99	1.75	16.7	0

Reaction conditions: Catalyst 1.0 g, Cellulose 1 g, H_2O 9 g, 12 h, $H_2/N_2 = 85/15$ (vol.%), 6.5 MPa. Catalyst pretreatment: see Table 1

[a] Pt: 1 wt%

[b] Pt 1 wt%, Re 2 wt%

[c] Si/Al_2

[d] Catalyst: 0.2 g

[e] Catalyst: 0.2 g, H_2O: 50 g, 2 h

[f] Yield = [(sum of C atoms in all products)/(total C atoms of cellulose introduced)] × 100

[g] Carbon selectivity = (moles products × number of carbon atoms in products)/(total moles of carbon atoms in products) × 100

[h] MeOH + EtOH + PrOH + BuOH + EG + PG

out at 573 K using Pt–Re/H-ZSM-5(23), which was effective for hydrocracking of triglycerides [3]. The selectivity to C2–C9 alkanes was as high as 76.8% with no CO_x formation, but the yield into alkanes and CO_x decreased to 51.8%. Also, at 543 K, the conversion and C2–C9 selectivities were 64.7 and 75.8% and other hydrocarbons and oxygenates were also detected. Thus, Pt-based catalysts were found to be effective for a direct hydrocracking of cellulose without any pretreatment.

Then, in order to improve carbon efficiencies into C2–C9 alkanes by reducing CH_4 and CO_x even at 673 K-reaction, biomass-derived materials were pretreated with C2–C6 alcohols such as 1-hexanol, prior to hydrocracking. Saka [1] has already reported that woody biomass can be successfully decomposed and liquefied in any supercritical alcohol and many kinds of oxygenates such as acetic acid and saccharides were formed.

First, organosolv-lignin commercially available from Aldrich Chemicals was pretreated. After 12 h-reaction at 673 K, gaseous and liquid products were analysed. As shown in Table 3, alkanes and CO_x were formed. Oxygen-containing products such as phenol, guaiacol were not detected by GC analysis.

The yield into (alkanes + CO_x) was affected by alcohols and the order of the yield was EtOH ≅ 1-propanol > 1-hexanol > 1-butanol. For 1-propanol, C2–C4 alkanes (50.1%) and C5–C9 alkanes (35.3%) were mainly formed with small amounts of other alkanes and CH_4 (3.27%)/CO_x

Table 3 Pretreatment with alcohol in hydrocracking of organosolv lignin

Alcohol	Yield into (alkanes + CO_x) (%)	Carbon selectivity (%)[a]					
		CH_4	C2–C4	C5–C9	C10–C20	C21+	CO_x
EtOH	100	8.34	32.5	44.7	6.88	0.62	6.93
1-Propanol	100	3.27	50.1	35.3	7.72	0.39	3.26
1-Butanol	74.2	2.46	52.9	37.9	4.12	0.46	2.16
1-Hexanol	88.2	3.56	41.6	45.8	5.41	1.20	2.38

Pretreatment: alcohol (10 mL) + organosolv lignin (1 g), Ar (2 MPa), 623 K, 2 h. Reaction conditions: pre-reduced 1 wt% Pt/H-ZSM-5 (23) (1 g) and H_2O (9 g), 673 K, 12 h, H_2/N_2 = 85/15 (vol.%), 6.5 MPa

[a] The yield and carbon selectivity: see Table 2

(3.26%). For other alcohols, C2–C4 and C5–C9 alkanes were also predominantly formed. Thus, pre-treatment by alcohol prior to hydrocracking was found to be effective for hydrocracking of organosolv-lignin to give C2–C9 alkanes.

Second, our interest is cellulose. As already mentioned in Table 2, a direct hydrocracking of cellulose produced large amount of CO_x and CH_4 with total selectivity of 39.7%, even in the presence of Pt/H-ZSM-5(23) catalyst. By pretreatment with alcohols, CH_4 and CO_x formations were dramatically reduced to approximately 1–4% selectivities, as shown in Table 4. The order of the yield into alkanes and CO_x were 1-pentanol $\cong$ 1-hexanol > 1-propanol > 1-butanol. For 1-hexanol, C2–C4 alkanes (42.1%) and C5–C9 alkanes (47.0%) were mainly formed with 4.86% of higher alkanes and CH_4 (3.10%)/CO_x (2.88%). For 1-butanol and 1-propanol, the selectivities to C2–C4 alkanes increased to 52.3 and 79.0%, while C5–C9 selectivities decreased to 38.5 and 15.7%. In these cases, the order of the kind of alcohol in pre-treatment of cellulose is found to be different from that of organosolv-lignin, as shown in Tables 3 and 4. Organosolv-lignin contains only lignin-like structure and, therefore, the lignin could dissolve even in ethanol and propanol. On the contrary, wood flour has much complex structures and it contains not only lignin, but also cellulose and hemicellulose structures. Therefore, alcohols with longer alkyl chain, probably, could be favorable for dissolving wood-like materials with higher molecular weight [1].

For 1-hexanol pre-treatment, the selectivity to higher carbon number compounds (C10+) was 4.86%, much lower than that from direct hydrocracking (C_{10+} = 20.9%), indicating that pre-treatment by alcohol may cause slightly preventing condensation reactions, but the condensation could still occur. Generally, it is well-known that zeolites would catalyze condensation of ethylene and ethanol to form propylene and butanes wit higher alkanes at 673–873 K [10]. So, even at high pressure conditions of hydrogen at 673 K, these condensations, probably, occur.

For two-step reaction using 1-hexanol, effects of catalyst support were examined, where Pt content was 1 wt%. The order of the yield into alkanes and CO_x were H-ZSM-5(23) > USY(5.3) > Y(5.1), in which the number in parenthesis denotes Si/Al_2 ratio. On the contrary, CH_4 and CO_x

Table 4 Pretreatment with alcohol in cellulose hydrocracking

Catalyst support	Alcohol	Yield into (alkanes + CO_x) (%)	Carbon selectivity (%)[b]					
			CH_4	C2–C4	C5–C9	C10–C20	C21+	CO_x
H-ZSM-5 (23)[a]	None	89.1	17.6	21.8	17.4	18.7	2.22	22.2
H-ZSM-5 (23)	1-Propanol	81.3	1.77	79.0	15.7	1.11	0.04	2.37
H-ZSM-5 (23)	1-Butanol	77.4	1.75	52.3	38.5	3.60	0.23	3.65
H-ZSM-5 (23)	1-Pentanol	100	3.27	37.0	45.9	10.1	0.49	3.23
H-ZSM-5 (23)	1-Hexanol	100	3.10	42.1	47.0	4.43	0.43	2.88
USY (5.3)	1-Hexanol	84.4	7.23	30.4	28.9	22.9	1.29	9.20
Y (5.1)	1-Hexanol	72.2	8.03	22.2	33.8	13.8	1.70	20.5

Pretreatment: alcohol (10 mL) + cellulose (1 g), Ar (2 MPa), 623 K, 2 h. Reaction conditions: 1 wt% Pt/support (1 g) and H_2O (9 g), 673 K, 12 h, H_2/N_2 = 85/15 (vol.%), 6.5 MPa

[a] Si/Al_2 ratio

[b] The yield and carbon selectivity: see Table 2

Table 5 Pretreatment with alcohol in hydrocracking of wood flour

Wood	Yield into (alkanes + CO_x) (%)	Carbon selectivity (%)[d]					
		CH_4	C2–C4	C5–C9	C10–C20	C21+	CO_x
Eucalyptus[a]	76.3	16.2	25.4	29.5	9.88	1.64	17.4
Eucalyptus[a, b]	33.4	15.8	20.4	11.7	4.34	2.85	44.9
Eucalyptus	100	2.59	42.6	46.8	5.74	0.54	1.69
Eucalyptus[c]	100	2.57	38.3	40.4	14.4	0.77	3.62
Japanese cedar (Hita)	92.4	3.10	37.1	37.3	19.5	1.32	1.71
Douglas fir	80.5	1.80	37.4	49.2	10.0	0.10	1.39

Pretreatment: 1-hexanol (10 mL) + wood flour (1 g), Ar (2 MPa), 623 K, 2 h. Reaction conditions: 1 wt% Pt/H-ZSM-5 (23) (1 g) and H_2O (9 g), 673 K, 12 h, H_2/N_2 = 85/15 (vol.%), 6.5 MPa

[a] No pre-treatment with 1-hexanol

[b] Reaction time is 1 h

[c] Pretreatment temperature: 543 K

[d] The yield and carbon selectivity: see Table 2

selectivities were in the order: Y(5.1) > USY(5.3) > H-ZSM-5 (23). Thus, the product selectivity would be associated with solid acid properties of catalyst supports, although further study is now in progress.

Third, alcohol pretreatment and successive hydrocracking of wood flour was carried out. As wood flour, Eucalyptus, Japanese cedar (Hita), and Douglas fir were used. As in the case of cellulose, a direct hydrocracking of Eucalyptus produced large amount of CO_x and CH_4 with total selectivity of 35.4%, even in the presence of Pt/H-ZSM-5 (23) catalyst and the yield into (alkanes and CO_x) were 76.3% after 12 h-reaction, as shown in Table 5. At 1 h-reaction of direct hydrocracking, the yield decreased to 33.4% and each alkane selectivity was lower than those after 12 h-reaction, except for C21+ selectivity. Figure 1 shows alkane product distributions in the 1- and 12 h-reactions. As the reaction proceeds, the yield of each alkane product increased, indicating that hydrocracking with deoxygenation of wood structure was found to be major reactions, but condensation could still occur under these conditions.

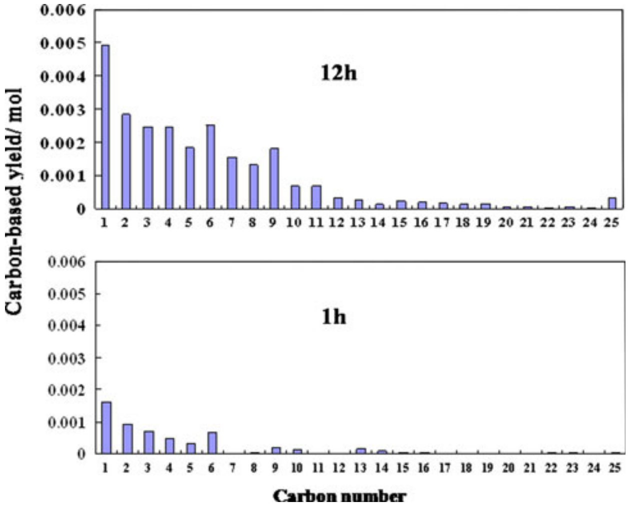

Fig. 1 Product distributions in direct hydrocracking of Eucalyptus. Eucalyptus(1 g), Cat.: 1 wt% Pt/H-ZSM-5 (23) (1.0 g), H_2/N_2 = 9/1, 6.5 MPa, H_2O (9 g), 673 K

By pretreatment with alcohols, CH_4 and CO_x formations were dramatically reduced to approximately 2–4% selectivities. The order of the yield into alkanes and CO_x was Eucalyptus > Japanese cedar (Hita) > Douglas fir. For Eucalyptus, C2–C4 alkanes (42.6%) and C5–C9 alkanes (46.8%) were mainly formed with 6.28% of higher alkanes and CH_4 (2.59%)/CO_x (1.69%). Pretreatment at 543 K resulted in slight decreases in C2–C4 and C5–C9 selectivities, but increase in C10–C20 selectivity. For Japanese cedar (Hita) and Douglas fir, the selectivities to C2–C4 alkanes slightly decreased to 37.1 and 37.4%, while C5–C9 selectivities were 37.3 and 49.2%.

Postulated scheme of decomposition pathway is shown in Fig. 2, where cellulose is chosen as a typical starting materials. By a direct hydrocracking of cellulose, C2–C9 alkanes and CH_4/CO_x are produced in 35 and 35% yields. Alcohol pretreatment could lead to lowering of molecular weight, by producing intermediates of, for example, monosaccharide and disaccharide [1], which are further converted to mainly C2–C9 alkanes by successive hydrocracking and condensation. By pretreatment using 1-hexanol, C2–C9 yields are dramatically increased to 89%, while CH_4/CO_x yields are reduced to only 6%. These findings suggest that the alcohol treatment of various cellulosic materials prior to catalytic hydrocracking can be extremely effective for improving selective formation of C2–C9 hydrocarbon, being useful for chemicals and liquid fuels without using fossil resources.

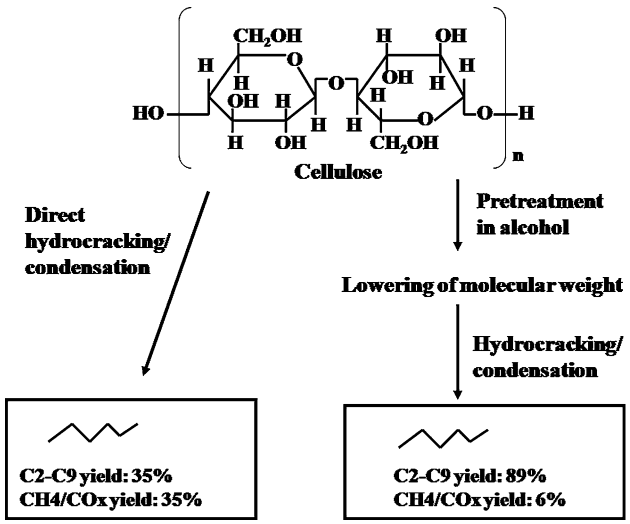

Fig. 2 Postulated scheme of cellulose hydrocracking

4 Conclusion

Pt/H-ZSM5 catalysts, which were active for glycerol reforming into propane and hydrotreating of triglycerides, were found to be active for hydrocracking of biomass-derived materials to form C2–C9 alkanes directly. Furthermore, by pre-treatment of these materials by alcohol such as 1-hexanol, prior to the hydrocracking, C2–C9 alkanes yields were found to be extremely improved. The pre-treatment of cellulose in 1-hexanol at 623 K, followed by hydrocracking catalyzed by Pt/H-ZSM-5(23) at 673 K, produced C2–C9 alkanes in 89% yields with CH_4/CO_x yields of only 6%, whereas, by direct hydrocracking of cellulose at 673 K, C2–C9 alkanes and CH_4/CO_x yields were formed in 35 and 35% yields, respectively. Combination of alcohol pre-treatment and Pt/H-ZSM-5-catalyzed hydrocracking was also effective for organosolv-lignin and wood flour. In Eucalyptus, C2–C9 alkanes yields were 89.4%. The reaction pathway involves lowering of molecular weight of cellulose materials, producing, probably, oxygenates intermediates such as mono-saccharide and disaccharide, which are further efficiently converted to alkane products by successive hydrocracking and condensation, catalyzed by Pt/H-ZSM-5. Co-feeding process of fossil-based heavy residue and biomass-based resources into chemicals and fuels would be feasible for a larger industrial scale, because biomass resources are much smaller scale than the fossil resources.

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