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Hydrocarbon Fuel Production from Lignocellulosic Biomass by Solvolysis and Catalytic Cracking

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Utilization of lignocellulosic biomass for alternative fuels requires efficient and low-cost processes for deoxygenation and conversion to hydrocarbons. We propose a 2-step biomass conversion process consisting of solvolysis pretreatment and co-processing with heavy petroleum oil in catalytic cracking. High liquefied yield (> 90 C%) was achieved by solvolysis in guaiacol and water with acetic acid catalysts. Bio-oil was mainly converted to gaseous hydrocarbons and coke by co-processing with model heavy oil (*n*-eicosane). Deoxygenation pathway to H₂O formation was accelerated by enhancing hydrogen-transfer activity even without supplying hydrogen. Hydrogen-transfer deoxygenation proceeded preferentially to olefin hydrogenation. Consequently, enhancing hydrogen-transfer activity in the co-processing of bio-oil and heavy petroleum oil was effective for efficient deoxygenation without lowering octane rating.

Keywords

Lignocellulosic biomass, Solvolysis, Catalytic cracking, Hydrogen transfer, Deoxygenation, Renewable fuel

1. Introduction

Lignocellulosic biomass is the most abundant type of natural resource and has potential as a feedstock for renewable fuels and chemicals. However, its energy density is much lower than that of petroleum-derived fuels because of its high oxygen content. Therefore, efficient and low-cost deoxygenation of biomass resources is required for conversion to hydrocarbons. The present study focused on the conversion of lignocellulosic biomass to liquid hydrocarbons that can be used as transportation fuels.

Many different processes have been investigated for liquefaction and upgrading of lignocellulosic biomass to liquid hydrocarbon fuels^{1)~8)}. However, some biomass upgrading processes such as hydrodeoxygenation^{5),9),10)} and biomass-to-liquid (BTL)¹¹⁾ are too expensive for utilization. The present study focused on the fluid catalytic cracking (FCC) process for biomass upgrading. FCC is one of the major oil refining

processes to convert heavy oil feedstocks into valuable light fractions such as gasoline. The FCC process should be economically more competitive than the hydrodeoxygenation and BTL processes because it can be operated at atmospheric pressure without supplying hydrogen. Co-processing of bio-oil with conventional crude oil in the FCC process has been widely studied recently^{5),12)~14)}.

Liquefaction pretreatment is one of the problems in biomass conversion with the FCC process. In most cases, flash pyrolysis is used to prepare the bio-oils supplied for co-processing with heavy petroleum oil in the FCC process. However, flash pyrolysis of lignocellulosic biomass, especially at high reaction temperature or high heating rate, forms polycyclic aromatic hydrocarbons (PAHs)^{15)~17)}, which are difficult to upgrade by the FCC process¹⁸⁾. In fact, co-processing of flash pyrolysis bio-oil and conventional feedstocks in the FCC process resulted in high coke yield and rapid catalyst deactivation^{13),19),20)}. Minimizing the effect of thermal cracking (pyrolysis) and maximizing the effect of catalytic cracking is fundamental for improving product selectivity in the FCC process²¹⁾.

In contrast, liquefaction pretreatment using a solvolysis process can produce bio-oil at a milder temperature (200–350 °C) than by pyrolysis (> 400 °C), thus avoiding the secondary condensation reaction and the

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formation of PAHs. On the other hand, the solvolysis process involves extra cost for the solvent which should be minimized. High liquefaction yields have been reported with phenolic solvents, such as phenol and guaiacol^{22)~24)}. These phenolic compounds are lignin components, so an inexpensive solvolysis process with high liquefied yield is expected to be achieved by recycling of the liquefied oil as a solvent. Solvolysis processes with the liquefied oil recycling system were previously investigated in the 1980s^{25)~27)}, but stable and continuous operation was not achieved. Recently, solvolysis of pinewood with solvent recycling was investigated, starting with guaiacol solvent which was gradually displaced by the liquefied products in the repeated solvolysis experiments^{24),28)~31)}. Steady-state liquefaction was achieved with high and constant liquid yield (90 C%) by fractionating the reactor effluents to light oil (recycled as solvent) and heavy oil (liquefaction product), but further investigation of solvolysis process is still required for cost reduction. This study focused on organic acids, which are by-products in biomass liquefaction. If these organic acids act as a catalyst in the solvolysis reaction, process cost will be reduced by lowering the reaction temperature and increasing liquid yield.

Deoxygenation selectivity presents another problem in biomass conversion with the FCC process. The FCC process is operated without supplying hydrogen, so hydrodeoxygenation producing H₂O is limited. However, the deoxygenation pathway producing CO₂ or CO results in serious carbon loss because of the high oxygen content of bio-oil (*ca.* 30 wt%)⁵⁾. In some literature, decreased CO₂ and CO yields occurred in the co-processing of oxygen-containing feedstocks with heavy petroleum oil^{32)~34)}. Suppression of CO₂ and CO formation and acceleration of H₂O formation can be achieved by the hydrogen-transfer reaction on Y zeolite catalyst. Part of the hydrogen atoms in the petroleum-based oil can be transferred to the oxygen-containing compounds in bio-oil and used for H₂O production. Recently, we found that activating the hydrogen-transfer reaction in the catalytic cracking of lipids is effective for acceleration of the deoxygenation pathway producing H₂O^{35)~37)}. Therefore, accelerating the hydrogen-transfer reaction in the co-processing of bio-oil and heavy petroleum oil is also expected to be effective for efficient deoxygenation without carbon loss even under H₂-free conditions.

The present study proposes a 2-step biomass conversion process consisting of solvolysis liquefaction pretreatment and co-processing of liquefied oil with heavy petroleum oil in an FCC process with enhanced hydrogen-transfer activity. The concept of this process is similar to that already proposed^{24),28)~31),38),39)}. In this paper, we report our recent investigations to improve the effectiveness of this process, especially the follow-

ing two points: Effect of organic acid catalysts on the low-temperature solvolysis of lignocellulosic biomass; and effect of the hydrogen-transfer activity of the FCC catalyst on deoxygenation selectivity and hydrocarbon composition produced in the co-processing of bio-oil and heavy petroleum oil.

2. Experimental

2.1. Liquefaction of Lignocellulosic Biomass

Model lignocellulose was prepared by mixing reagent powders of cellulose (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and dealkaline lignin (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) in the weight ratio of 60 : 40. The mixture was ground with a planetary ball mill and sieved to particles between 75 μm and 106 μm. Powder of Japanese cedar was also prepared with the same procedure.

Solvolysis experiments were carried out using a batch autoclave reactor with an internal volume of 430 mL. The model lignocellulose or Japanese cedar powder was mixed with acetic acid (Wako Pure Chemical Industries, Ltd.), guaiacol (Tokyo Chemical Industry Co., Ltd.), and water. Acetic acid was used as a model organic acid. The mixture was loaded into the autoclave and mechanically stirred. After flushing with N₂ at 1 MPa at room temperature, the reactor was sealed and heated to reaction temperature over 30 min. After the desired reaction time, the reactor was spontaneously cooled to room temperature over approximately 90 min and the gaseous products were collected in a gas sampling bag. The liquid and solid products were collected and separated by filtration. The solid residue remaining on the reactor wall and filter paper was washed with acetone and dried in a vacuum. The eluted products were collected by removing acetone with vacuum evaporation and added to the liquid products.

Mass balances of higher than 80 wt% of the total intake (including solvent, water, and acetic acid) were obtained in all solvolysis experiments. Gaseous products were analyzed using a gas chromatography (GC) system (GC-8A, Shimadzu Corp., Kyoto, Japan) equipped with a packed column (SHINCARBON-ST 50/80, Shinwa Chemical Industries, Ltd., Kyoto, Japan) and a thermal conductivity detector (TCD) with Ar as the carrier gas. The elemental composition of the solid products was determined with an NC analyzer (SUMIGRAPH NC-1000, Sumika Chemical Analysis Service, Ltd., Osaka, Japan). Gaseous, liquid and solid yields were calculated as the carbon-fraction of biomass feedstock with Eqs. (1)-(3) assuming that all gaseous and solid products were produced from the lignocellulose feedstock, not from the guaiacol solvent or organic acid catalysts.

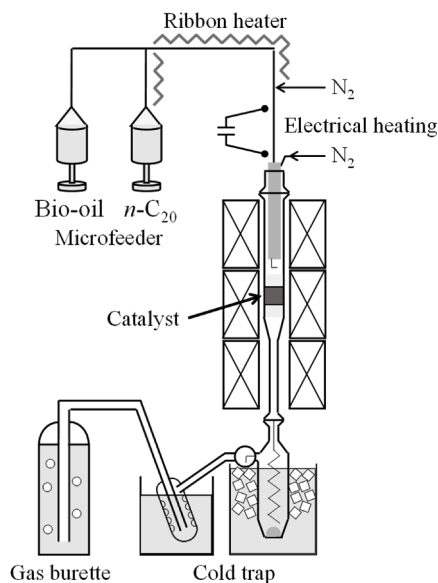


Fig. 1 Schematic Diagram of the Microactivity Test Reactor with Two Injection Lines Used for Co-processing Experiments

$$Y_{\text{solid}} = \frac{M_{\text{solid}}}{M_{\text{lignocellulose intake}}} \times 100 \quad (1)$$

$$Y_{\text{gas}} = \frac{M_{\text{gas}}}{M_{\text{lignocellulose intake}}} \times 100 \quad (2)$$

$$Y_{\text{liquid}} = 100 - (Y_{\text{solid}} + Y_{\text{gas}}) \quad (3)$$

2. 2. Co-processing of Bio-oil and Heavy Oil Model Compound in Catalytic Cracking

Liquid products from solvolysis of lignocellulose were co-processed with a model heavy oil in a fixed bed microactivity test reactor. The model heavy oil used *n*-eicosane (*n*-C₂₀; Tokyo Chemical Industry Co., Ltd.). Catalytic cracking catalysts for the experiments were either equilibrium catalysts (E-cat) or hydrothermally deactivated catalysts. E-cat was obtained from a commercial residue fluid catalytic cracking (RFCC) process, and the hydrothermally deactivated catalysts were prepared from fresh RFCC catalyst using a fluidized bed reactor under 100 % steam atmosphere at 800 °C. Hydrothermally deactivated catalysts with different catalytic activities were prepared by varying the steam deactivation time. The catalysts were characterized by X-ray diffraction (XRD) using a RINT 2550 (Rigaku Corp., Tokyo, Japan) with Cu K α radiation. The unit cell size (UCS) of the Y zeolite contained in each catalyst was calculated from the diffraction peaks of the (533) and (642) planes following the method outlined in ASTM D3942-03.

Figure 1 shows the schematic diagram of the experimental setup for co-processing. Catalysts (4 g) were placed in the reactor maintained at the reaction temperature. Bio-oil and *n*-C₂₀ were fed into the reactor using two independent syringe pumps. The feeding line

of *n*-C₂₀ was heated to higher than 80 °C with a ribbon heater, whereas that of bio-oil was not heated because the bio-oil was unstable at high temperature. The two feedstocks were mixed and heated electrically in a pre-heating line to the reaction temperature. The weight ratio of bio-oil to *n*-C₂₀ was varied from 0 : 100 to 30 : 70. The feed injection time was 75 s and the weight hourly space velocity (WHSV) was 16 h⁻¹, corresponding to the weight ratio of catalyst to feedstock oil (Cat/oil) of 3 g/g. N₂ gas was added during feed injection at 19 mL min⁻¹. After each run, the catalyst was stripped by purging with N₂ gas at 5 mL min⁻¹ for 15 min. During the reaction and stripping stages, the liquid products were collected in a cold trap with two receiving vessels connected in series and maintained at 0 and -15 °C, respectively. Simultaneously, the gaseous products were collected in a gas burette by displacement of a saturated NaCl solution. The mass balance across the collected products was in the range of 94-107 wt% of the process inputs for all catalytic cracking experiments.

The amounts of H₂, N₂, CO₂, and CO in the gaseous products were determined using a GC-TCD with the same procedure used for gaseous product analysis in the solvolysis experiments. Hydrocarbons and oxygenates were analyzed with another GC system (GC-2014, Shimadzu Corp.) equipped with a capillary column (BP1, SGE Analytical Science Pty. Ltd., Victoria, Australia) and a flame ionization detector (FID) with He as the carrier gas. Biphenyl (99.5 %, Sigma-Aldrich Co.) was used as an internal standard in the GC-FID assay. Quantification of the hydrocarbons and oxygenates was based on the effective carbon number theory⁴⁰. The hydrocarbon products were classified into the gaseous hydrocarbon fraction (C₁-C₄) and the liquid hydrocarbon fraction (C₅-). The oxygenates in the liquid products were also analyzed using a gas chromatography-mass spectrometry (GC-MS) system (GCMS-QP2010 Plus, Shimadzu Corp.) equipped with a capillary column (Rxi-1ms, Restek Corp., Bellefonte, PA, USA) with He as the carrier gas. The amount of coke deposited on the catalyst was determined from the difference in the weights of the reactor before and after the catalytic test.

3. Results and Discussion

3. 1. Liquefaction of Lignocellulosic Biomass

3. 1. 1. Effect of Solvolysis Reaction Conditions

Solvolysis of lignocellulosic biomass under various reaction conditions (temperature, time, and catalyst and lignocellulose loadings) was investigated to prepare bio-oil suitable for co-processing in the FCC process. Firstly, the effect of reaction temperature on the product yields was investigated as shown in Fig. 2(a). The liquid yield reached a maximum at 200 °C.

At temperatures lower than 200 °C, the yield of gaseous products was low (< 4 C%) and the main component was CO₂. As shown in **Fig. 2(b)**, the solid product was gray with carbon content of approximately 46 wt%, which is consistent with the carbon content of the model lignocellulose feedstock. This result suggests that some of the solid feedstock was not converted and remained unchanged. Therefore, liquefaction will still proceed by enhancing the severity of the reaction conditions such as longer reaction time and use of catalysts.

At temperatures higher than 250 °C, the gaseous yield increased to higher than 10 C%. In addition to CO₂, small amounts of CO and CH₄ were formed. As shown in **Fig. 2(c)**, the solid product was black with carbon content much higher (69 wt% and 74 wt% at 250 °C and 300 °C, respectively) than that of the feedstock, which suggests coke formation by a condensation reaction. Formation of CH₄ and coke at high temperature indicates progress of pyrolytic decomposition which produces bio-oil that is highly condensed and difficult to upgrade in the FCC process.

These findings suggest that enhancing liquefaction at temperatures lower than 200 °C is preferable for producing bio-oil that is easy to handle in the following FCC process. Therefore, the effect of the reaction time and the use of catalysts to accelerate the solvolysis

at low temperature (< 200 °C) were investigated. **Figures 3(a)** and **3(b)** show the effect of reaction time and catalyst concentration, respectively, at 200 °C. As expected, longer reaction time enhanced liquefaction and increased liquid yield. Using an organic acid catalyst was much more effective to increase liquefaction. Liquid yield of higher than 90 C% was achieved with only 1 wt% addition of acetic acid, whereas addition of excess acetic acid (*e.g.* 10 wt%) decreased liquid yield and increased solid yield. The reason for the decrease in liquid yield with 10 wt% acetic acid may be that the excess acidity can catalyze the condensation and re-polymerization of the liquefied products^{29),41)}. Here, organic acids are well-known by-products in biomass liquefaction. Therefore, liquefaction by solvolysis at low temperature can be accelerated by appropriate recycling of the organic acids in the liquid products.

The effect of the lignocellulose loading on liquefaction was also investigated as shown in **Fig. 3(c)**. Liquid yield of higher than 90 C% was achieved with lignocellulose loading as high as 30 wt%. However, solid yield increased to 16 C% and liquid product with very high viscosity was obtained with lignocellulose loading of 40 wt%. The low reactivity with 40 wt% of lignocellulose may be due to insufficient contact between the bulky lignocellulose and solvent because the apparent volume of the lignocellulose powder feedstock was much larger than that of the solvent under this condition. In addition, the high viscosity of the liquefied product could have decreased the reactivity for further liquefaction.

3. 1. 2. Comparison of Model Lignocellulose and Actual Biomass

Solvolysis was compared for model lignocellulose (mixture of reagent cellulose and lignin) and actual biomass (Japanese cedar). **Table 1** summarizes the gaseous, liquid and solid yields in each experiment. Addition of 1 wt% acetic acid was also effective for liquefaction of Japanese cedar. Solvolysis of Japanese cedar showed a similar trend to model lignocellulose feedstock, suggesting that the results obtained from the investigation with model lignocellulose can be extended to the solvolysis of actual biomass.

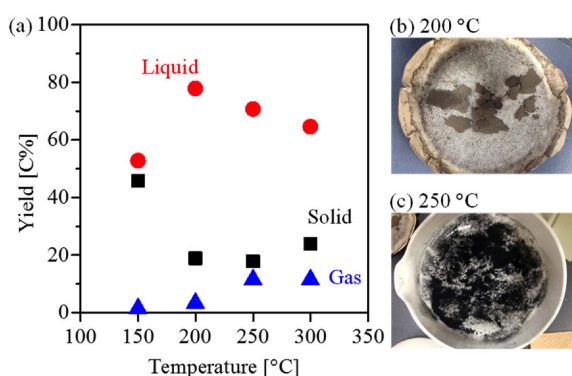
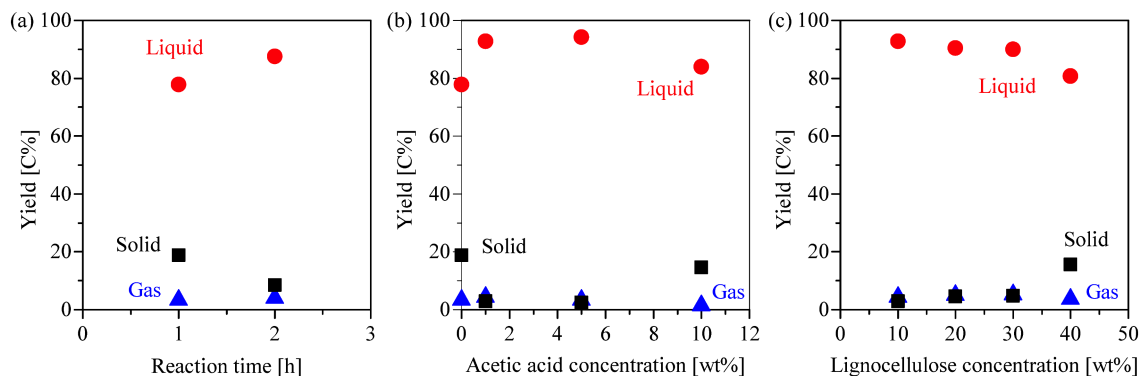


Fig. 2 (a) Carbon-based Yields of Gaseous, Liquid and Solid Products of Solvolysis at Different Temperatures (lignocellulose/guaiacol/water = 10/85/5 (wt%), reaction time: 1 h), (b) Solid Product of Solvolysis at 200 °C, and (c) Solid Product of Solvolysis at 250 °C

Table 1 Feedstock Composition and Carbon-based Yields in Solvolysis of Model Lignocellulose and Japanese Cedar (reaction temperature: 200 °C, reaction time: 1 h)

| Cellulose + Lignin (model lignocellulose) | Feedstock composition [wt%] | | | | Carbon-based yield [C%] | | |
|--|-----------------------------|-------------|----------|-------|-------------------------|--------|-------|
| | Japanese cedar | Acetic acid | Guaiacol | Water | Gas | Liquid | Solid |
| 10 | - | 0 | 85 | 5 | 3.3 | 77.9 | 18.8 |
| 10 | - | 1 | 84 | 5 | 4.3 | 92.7 | 2.9 |
| - | 10 | 0 | 85 | 5 | 4.2 | 75.3 | 20.5 |
| - | 10 | 1 | 84 | 5 | 6.5 | 90.2 | 3.3 |



(a) Effect of reaction time (lignocellulose/guaiacol/water = 10/85/5 (wt%), reaction temperature: 200 °C). (b) Effect of acetic acid concentration (lignocellulose/acetic acid/guaiacol/water = 10/ x /(85 - x)/5 (wt%), reaction temperature: 200 °C, reaction time: 1 h). (c) Effect of lignocellulose concentration (lignocellulose/acetic acid/guaiacol/water = x /1/(94 - x)/5, reaction temperature: 200 °C, reaction time: 1 h).

Fig. 3 Carbon-based Yields of Gaseous, Liquid and Solid Products of Solvolysis

Table 2 Feedstock Composition and Yields of Oxygen-containing Products in Co-processing of Bio-oil and n -C₂₀ on E-cat (reaction temperature: 500 °C, WHSV: 16 h⁻¹)

| Bio-oil : n -C ₂₀ (weight ratio) | Feedstock composition [wt%] | | | Product yield [wt%] | | |
|--|---|-------|----------------------|------------------------------|-----------------|-----|
| | Oxygen-containing organic compounds (average composition: C/H/O = 63/7/30 (wt%)) | Water | n -C ₂₀ | Oxygenates (alkylphenols) | CO ₂ | CO |
| 20 : 80 | 19.0 | 1.0 | 80.0 | 2.1 | 0.2 | 0.5 |
| 30 : 70 | 28.5 | 1.5 | 70.0 | 2.7 | 0.5 | 0.8 |

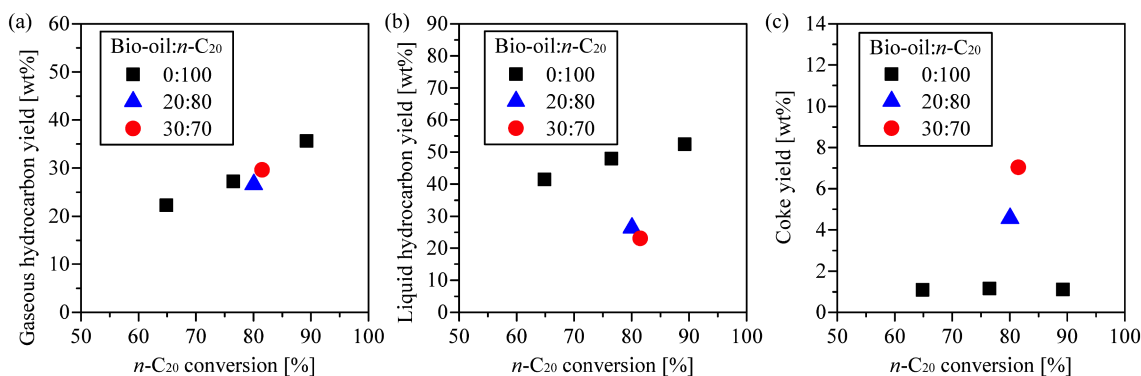


Fig. 4 Yields of (a) Gaseous Hydrocarbons, (b) Liquid Hydrocarbons, and (c) Coke from Co-processing of Bio-oil and n -C₂₀ by Catalytic Cracking on E-cat (reaction temperature: 500 °C (co-processing of bio-oil and n -C₂₀) or 450-500 °C (single catalytic cracking of n -C₂₀), WHSV: 16 h⁻¹)

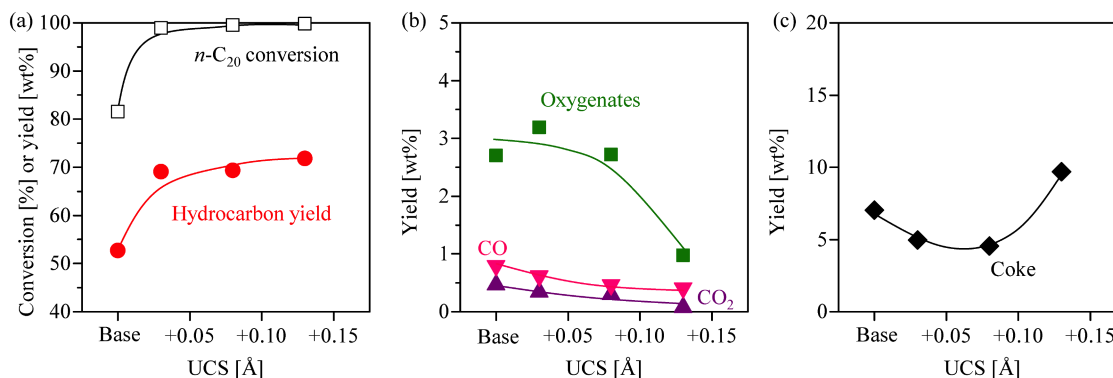
3.2. Co-processing of Bio-oil and Model Heavy Oil by Catalytic Cracking

3.2.1. Reaction Products in Co-processing

Co-processing of bio-oil and heavy oil in the catalytic cracking reaction was investigated. The bio-oil was prepared by solvolysis with the following reaction conditions: model lignocellulose/acetic acid/guaiacol/water 30/1/64/5 (wt%), reaction temperature 200 °C, and reaction time 1 h. The liquid product obtained was a single-phase black liquid with liquid yield of 90.0 C% as shown in Fig. 3(c). From this result, the composi-

tion of the bio-oil/ n -C₂₀ mixtures (20 : 80 or 30 : 70 by weight) used for the co-processing feedstock can be roughly calculated as shown in Table 2, assuming that the C/H/O ratio did not change during the liquefaction. The mixtures were fed into the catalytic cracking reactor and the reaction products were analyzed. For comparison, single catalytic cracking of n -C₂₀ (bio-oil : n -C₂₀ = 0 : 100) was also investigated.

Figure 4 shows the yield of gaseous hydrocarbons, liquid hydrocarbons, and coke. The conversion of n -C₂₀ was varied by the reaction temperature. n -C₂₀



(a) n -C₂₀ conversion and hydrocarbon yield, (b) Yields of oxygenates, CO₂ and CO, (c) Coke yield.

Fig. 5 Conversion and Reaction Product Yields from the Co-processing of Bio-oil and n -C₂₀ by Catalytic Cracking on FCC Catalysts with Different UCS (bio-oil : n -C₂₀ = 30 : 70, reaction temperature: 500 °C, WHSV = 16 h⁻¹)

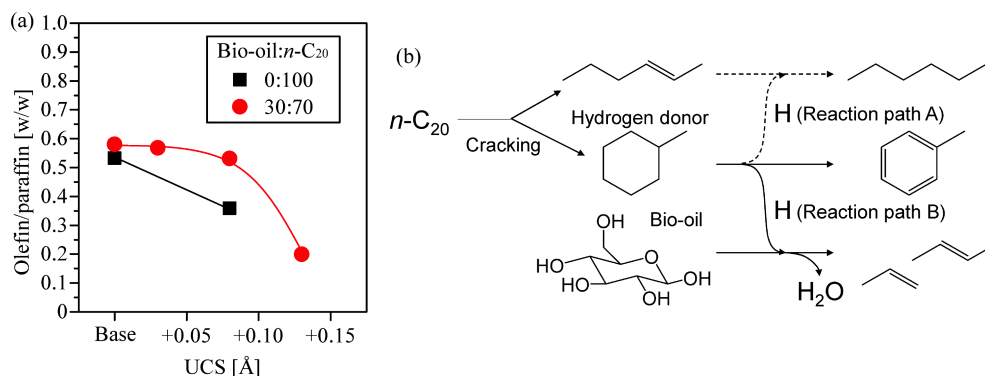
conversion in the co-processing experiments (*ca.* 80 %) was lower than that in the single cracking of n -C₂₀ (89 %) at the same reaction temperature (500 °C). Reduced conversion by co-processing was also reported previously^{19),20),42)}. Co-processing of bio-oil and n -C₂₀ produced similar gaseous hydrocarbon yield, lower liquid hydrocarbon yield, and higher coke yield than single cracking of n -C₂₀ at similar n -C₂₀ conversion. It should be noted that the amount of n -C₂₀ in the feedstock of the co-processing experiments is lower than that of the single n -C₂₀ cracking experiment. Therefore, the result in Fig. 4 suggests that the bio-oil was mainly converted to gaseous hydrocarbons and coke, consistent with previous findings⁴³⁾. More efficient cracking avoiding coke formation will require lower molecular weight of bio-oil in the pretreatment liquefaction step, which will be investigated in our future work.

The progress of deoxygenation during catalytic cracking was also confirmed from the yields of oxygen-containing products, as shown in Table 2. The produced oxygenates consisted of alkylphenols, but with yields lower than 3 wt%, although the feedstock contains 19.0 wt% or 28.5 wt% of oxygen-containing organic compounds. The yields of CO₂ and CO were also very low. In addition, the carbon contents of the coke produced by co-processing and single n -C₂₀ cracking was almost the same (85-89 wt%), suggesting that little oxygen was contained in the coke products. These results indicate that most oxygen atoms contained in the feedstock were removed as H₂O even without supplying H₂. Formation of H₂O was observed in the liquid product of the co-processing experiments, but unfortunately was not quantified. The H₂O yield can be estimated as approximately 7-10 wt% from calculation of the oxygen balance. H₂O formation can be attributed to the hydrogen-transfer reaction between the hydrogen-donor produced by the n -C₂₀ cracking and the oxygen-containing products.

3. 2. 2. Effect of Hydrogen-transfer Reaction

Co-processing of bio-oil and n -C₂₀ on catalysts with different activity was investigated. The effect of the hydrogen-transfer activity of the FCC catalysts on the deoxygenation reaction and produced hydrocarbon composition was especially evaluated. FCC catalysts containing Y zeolites with different UCS were prepared by steam deactivation of fresh FCC catalyst. Here, the UCS has a direct relationship with the relative amounts of silicon and aluminum in zeolites because aluminum atoms are larger than silicon atoms⁴⁴⁾. On the other hand, the hydrogen-transfer activity of the Y zeolite catalyst depends on the density of aluminum sites in the unit cell^{45)~47)}. Therefore, the UCS of the Y zeolites in the FCC catalysts can be used as an index of hydrogen-transfer activity^{48)~50)}, as Y zeolite with larger UCS shows higher hydrogen-transfer activity.

Figure 5 shows the conversion of n -C₂₀ and the yields of hydrocarbons, oxygenates, CO₂, CO, and coke from the co-processing of bio-oil and n -C₂₀ on FCC catalysts with different UCS. The base UCS on the horizontal axis corresponds to E-cat, and all steam deactivated catalysts showed larger UCS. Hydrocarbon yield increased and oxygenate yield decreased with higher UCS, suggesting involvement of the deoxygenation reaction. However, the yields of CO₂ and CO also decreased with higher UCS, suggesting that the selectivity of the deoxygenation pathway for H₂O was accelerated on the FCC catalyst with large UCS. In other words, the high hydrogen-transfer activity of the FCC catalyst promotes deoxygenation producing H₂O. As mentioned in the 1. Introduction, deoxygenation to H₂O is an efficient pathway because all carbon resources contained in the biomass feedstock can be converted to hydrocarbons whereas deoxygenation to CO₂ or CO results in partial carbon loss. Consequently, acceleration of the hydrogen-transfer reaction is effective for efficient conversion of bio-oil to hydrocarbons in co-



Reaction pathway A is the conventional hydrogen-transfer reaction in the heavy oil cracking. Reaction pathway B is the hydrogen-transfer deoxygenation forming H_2O . The result shown in (a) suggests that the reaction pathway B proceeds more preferentially in co-processing of bio-oil and $n\text{-C}_{20}$.

Fig. 6 (a) Olefin/paraffin Ratio from the Co-processing of Bio-oil and $n\text{-C}_{20}$ by Catalytic Cracking on FCC Catalysts with Different UCS (reaction temperature: $500\text{ }^\circ\text{C}$, WHSV: 16 h^{-1}), (b) Proposed Reaction Pathway of Hydrogen-transfer Reaction

processing with heavy oil feedstock in the FCC process.

Although the hydrogen-transfer reaction was confirmed to be effective for efficient deoxygenation of bio-oil, the hydrogen-transfer reaction has a disadvantage in the FCC process in petroleum refinery: it reduces the gasoline octane rating by converting olefins to paraffins. In fact, the hydrogen-transfer activity of FCC catalysts has been suppressed in recent catalyst design¹⁴. Therefore, if the hydrogen-transfer activity is enhanced in the co-processing of bio-oil and heavy oil, the selectivity of the hydrogen acceptor (olefin or oxygenates) is important for the quality of the produced hydrocarbon fuel.

Figure 6 shows the olefin/paraffin ratio in the products from the co-processing of bio-oil and $n\text{-C}_{20}$ and from single $n\text{-C}_{20}$ cracking on different FCC catalysts. The olefin/paraffin ratio decreased with increase in the UCS of the zeolite in single $n\text{-C}_{20}$ cracking, due to the hydrogen-transfer reaction. Here, the hydrogen donor is naphthenes formed by $n\text{-C}_{20}$ cracking, and the hydrogen species released from the hydrogen donor are received by the olefins (Fig. 6(b), reaction path A). In contrast, the olefin/paraffin ratio was almost constant on FCC catalysts with UCS ranging from base to base + $0.08\text{ } \text{Å}$ ($1\text{ } \text{Å} = 10^{-10}\text{ m}$) in co-processing of bio-oil and $n\text{-C}_{20}$, attributed to the strong hydrogen-accepting ability of oxygen-containing compounds in the bio-oil. Therefore, the hydrogen species released from the hydrogen donor are preferentially received by the oxygen-containing compounds to form H_2O (Fig. 6(b), reaction path B) rather than by the olefins to form paraffins. This trend is consistent with the result obtained in the catalytic cracking of triglycerides in our previous study³⁷. Consequently, enhancing hydrogen-transfer activity in the co-processing of bio-oil and heavy oil was confirmed to be effective for efficient deoxygenation

without affecting the octane rating.

On the other hand, excess hydrogen-transfer activity (e.g. UCS = base + $0.13\text{ } \text{Å}$) results in coke formation (Fig. 5(c)) and olefin hydrogenation (lower olefin/paraffin ratio in Fig. 6(a)). Therefore, optimizing the hydrogen-transfer activity is important for achieving efficient deoxygenation and high yield of valuable hydrocarbons.

4. Conclusion

The present study investigated the conversion of lignocellulosic biomass to hydrocarbon fuels with a 2-step process: liquefaction by solvolysis followed by co-processing of liquefied biomass with heavy oil in the FCC process. Addition of 1 wt% organic acids was confirmed to be effective for high liquid yield in solvolysis at low reaction temperature. Organic acids are by-products of biomass liquefaction, so efficient solvolysis can be achieved by recycling the organic acids in the liquid products. Bio-oil was mainly converted to gaseous hydrocarbons and coke in co-processing with model heavy oil. Deoxygenation forming H_2O rather than CO_2 or CO was accelerated even without supplying hydrogen by enhancing the hydrogen-transfer activity of the FCC catalyst. Hydrogen-transfer deoxygenation proceeded preferentially to hydrogenation of olefins, which results in the suppression of octane rating loss even on FCC catalyst with enhanced hydrogen-transfer activity.

Acknowledgment

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Nomenclatures

| | | |
|-------|---|------|
| M_i | : total mass of the carbon in the component i | [g] |
| Y_i | : carbon-based yield of the component i | [C%] |

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要 旨

加溶媒分解と接触分解による木質バイオマスからの炭化水素燃料製造

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木質バイオマスの石油代替燃料としての利用には、効率的かつ安価な脱酸素化により炭化水素に転換することが求められる。本論文では、加溶媒分解前処理および重質油との混合接触分解からなる2段階プロセスを提案し、これまでの検討結果を報告した。加溶媒分解では、グアイアコールおよび水を溶媒とし、酢酸触媒を用いて90 C%以上の液化を達成した。加溶媒分解で得られた液体生成物と重質油モデル物質 (*n*-エイコサン) の混合接触分解では、バイオオイルは主に気体炭化水素とコー

クに転換された。また、水素移行活性を高めることで、水素を反応場に供給していないにもかかわらず H₂O を生成する脱酸素経路が促進された。さらに、水素移行反応による脱酸素化はオレフィン類の水素化よりも優先して進行することを確かめた。この結果より、バイオオイルと重質油の混合接触分解において水素移行活性を高めることで、オクタン価の低下を抑制しつつ効率的な脱酸素化が達成できることが示唆された。

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