1. Introduction

Current consumption of petroleum-derived transportation fuels has resulted in large increases in \( \text{CO}_2 \) emissions worldwide. Adoption of biomass-derived fuels (so-called biofuels) are expected to decrease total carbon emissions because biomass absorbs previously emitted \( \text{CO}_2 \) during the growth process. However, biofuels currently have higher production costs and lower production capacity compared to petroleum-based fuels. Present practical applications of biofuels are limited to blending biofuels into petroleum-derived fuels for use in conventional engines. Hydrocarbons are the most desirable components of transportation biofuels because conventional engines are designed to operate using hydrocarbons as the fuel. Biofuels consisting of hydrocarbons are called as “drop-in” biofuels because use is directly possible in conventional engines without the need for costly modifications.

Industrial atmospheric distillation of crude petroleum obtains a series of products including gas (gas product from overhead, consisting of \( \text{CH}_4 \) and \( \text{C}_2 \) hydrocarbons), liquefied petroleum gas (LPG) (liquid product from overhead, consisting of \( \text{C}_3 \) and \( \text{C}_4 \) hydrocarbons), gasoline distillate (or so-called naphtha distillate, evaporating between 308-453 K), kerosene distillate (evaporating between 443-523 K), diesel distillate (evaporating between 513-623 K), and heavy oil (atmospheric residue).

Gasoline and diesel distillates are currently used as fuels for automobiles. Commercial gasoline is a mixture of \( \text{C}_5 \)-\( \text{C}_{10} \) hydrocarbons and diesel is a mixture of \( \text{C}_{11} \)-\( \text{C}_{20} \) hydrocarbons. Branched hydrocarbons (isoparaffins) have high octane numbers and are suitable for gasoline engines without the risk of detonation. Linear hydrocarbons (\( n \)-paraffins) have high cetane numbers and are suitable for diesel engines because the fuel is not compressed. In addition, LPG has considerable potential as a green and sustainable fuel for automobiles fitted with Autogas engines.

Production of hydrocarbon-based bio-jet fuel (for airplanes) has recently become an important field in the biofuel research. The worldwide market for gasoline
in the world is expected to contract due to the promotion of electric vehicles. However, the market for jet fuel will increase because of the high energy density required for the jet engine. Current jet fuel (so-called aviation kerosene) is a mixture of kerosene-range hydrocarbons (C9-C15 or C10-C15) but the freezing point is very low (≤233 K) to preserve the liquid state at the very low temperatures at high altitudes. Current jet fuel contains many branched hydrocarbons with low freezing points. Fatty acid methyl ester (FAME) produced by the transesterification of vegetable oil with methanol has been assessed as a bio-jet fuel in trial flights. The FAME molecules necessarily retain some C=C bonds to decrease the freezing point but also reduce the anti-oxidation characteristics of the fuel. Moreover, any C=O bonds in the FAME molecules decrease the combustion efficiency. Therefore, FAME must be replaced by hydrocarbon-based bio-jet fuel to ensure flight safety.

The BTL (biomass to liquid fuel) process and the hydrotreatment process are the main industrial processes currently used to produce hydrocarbon biofuels. Recently, conversion of algae oil to jet fuel (so-called ATJ process) and conversion of bioethanol to jet fuel (so-called ETJ process) have attracted considerable interest worldwide. This review paper introduces the main reactions adopted in these processes for converting various biomass feedstocks to LPG, gasoline, diesel, and jet fuel.

2. Catalytic Reactions for Conversion of Synthesis Gas to Liquid Fuels

2.1. Routes for Conversion of Woody Biomass to Liquid Fuels

Figure 1 shows the biochemical route and the thermochemical route for the conversion of woody biomass to liquid fuels. The biochemical route uses sugars as the substrate and the thermochemical route uses syngas (syngas, a mixture of carbon monoxide and hydrogen) as the substrate. Thermochemical conversion includes the gasification step and the liquefaction step. The woody biomass is converted to syngas in the gasification step and the formed syngas is converted to liquid fuels in the liquefaction step. The thermochemical route has two advantages compared to the biochemical route. Firstly, lignin cannot be saccharified in the biochemical route, but can be gasified to syngas in the thermochemical route. Consequently, all components of the woody biomass can be utilized in the thermochemical route. Secondly, the biochemical route only produces alcohols (mainly bioethanol), but the thermochemical route produces various compounds (hydrocarbons, alcohols, and others) from the syngas. Moreover, the biogas obtained from methane fermentation process (a mixture of CH4 and CO2) can also be converted to syngas by methane dry reforming. Consequently, the utilization of syngas is an important field in biomass research. This section focuses on the catalytic conversion of syngas to hydrocarbons and mixed alcohols.

2.2. Conversion of Syngas to Hydrocarbons by Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis (F-T synthesis) is an important reaction to produce hydrocarbons from syngas. Carbon monoxide reacts with hydrogen to form mixed hydrocarbons and water (Eq. (1)).

\[ n\text{CO} + (2n + 1)\text{H}_2 = \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \]  

Figure 2 shows the simplified reaction mechanism of the F-T synthesis. The C=O bond of a CO molecule (absorbed on the catalyst surface) is cleaved to form a C* active species and an O* active species. The O* species reacts with a H2 molecule to form a H2O molecule and the C* species reacts with a H2 molecule to form a CH2* species. The formed CH2* species polymerizes to 1-olefin (CH2=CH2). The formed (CH2)n react with H2 to form paraffin. The key step in the F-T synthesis is the polymerization of the CH2* intermediate to 1-olefin (CH2=CH2). The n value in (CH2)n cannot be controlled in a typical F-T synthesis because the polymerization degree cannot be controlled once the polymerization reaction starts. The F-T synthesis produces CnH2n+2 in which the n value ranges from 1 to over 100 based on the local thermodynamics. Consequently, the CnH2n+2 products consist of gases (1 ≤ n ≤ 4), liquids (5 ≤ n ≤ 20), and solids (n > 20) at room temperature.

According to the CH2* polymerization mechanism, the proportion of each hydrocarbon product among the total hydrocarbons obeys an Anderson-Schultz-Flory (A-S-F) distribution. The chain growth probability \( \alpha \) is defined as a ratio of the (CH2)n* which reacted to form (CH2)n+1* to the total (CH2)n*. The parameter \( \alpha \) ranges between 0 to 1 because some (CH2)n* intermediates are desorbed from the catalyst surface in each step. The \( \alpha \) value is about 0.60-0.65 on Fe-based cat.
alysts, about 0.80-0.85 on Co-based catalysts, and about 0.88-0.91 on Ru-based catalysts. Co-based catalysts are usually used in large-scale plants based on the catalytic activity and price\(^1,2\). The development of novel Ru-based catalysts to achieve high catalytic activity is a topic of lab-scale research\(^4\)\(^_{12}\).

\(\text{C}_{20}\) solid hydrocarbons (called F-T waxes) are formed in the F-T synthesis. The F-T reaction in a gas-flow fixed-bed reaction system carried out by introducing syngas to a tube reactor filled with solid catalyst results in the F-T waxes remaining in the reaction tube, covering the catalyst surface, and resulting in catalyst deactivation. Consequently, a gas-flow slurry-phase reaction system is used for the F-T synthesis. Figure 3 shows the schematic diagram of two stirred slurry reactors for the F-T synthesis.

**Figure 3** Schematic Diagram of Two Stirred Slurry Reactors for the F-T Synthesis

Table 1 lists the results of F-T synthesis in the 12.5 L bench-scale reactor over Mn-Zr-Co/SiO\(_2\) catalyst at 513 K under 3 MPa\(^{\text{a)}}\).

| Run | Solvent          | Conv. [%] | Select. for C\(_5\) [\%] | \(\alpha\) \(^{\text{b)}}\) |
|-----|------------------|-----------|--------------------------|------------------|
| 1   | \(n\)-C\(_{16}\)H\(_{34}\) | 70.7      | 83.0                     | 0.86             |
| 2   | \(n\)-C\(_{14}\)H\(_{30}\) | 71.3      | 79.3                     | 0.85             |
| 3   | Diesel\(^{\text{c)}}\) | 68.8      | 85.6                     | N.A.             |
| 4   | F-T crude oil\(^{\text{d)}}\) | 72.3      | 80.6                     | N.A.             |

\(<\text{a)}\text{ Catalyst: 125 g; Co loading: 20 wt\%; Zr loading: 2 wt\%; Mn loading: 2 wt\%; solvent: 4 L; input gas: 30 \% CO + 60 \% H\(_2\) + 10 \% N\(_2\); gas flow rate: 20 L min\(^{-1}\); stirring speed: 700 rpm.}\>

\(<\text{b)}\text{ Chain growth probability, calculated from A-S-F distribution.}\>

\(<\text{c)}\text{ Purchased from petrol station.}\>

\(<\text{d)}\text{ Collected from the tube in the middle portion of the 12.5 L reactor.}\>

Adapted from ref. 1). Copyright (2009) ELSEVIER.

CO conversion significantly increased by agitation in the slurry-phase F-T synthesis. The shape of the slurry reactor also influenced CO conversion. CO conversion obtained in the 12.5 L reactor was higher than that obtained in the 0.5 L reactor at the same W/F value. The 12.5 L reactor (IH/ID: 16) had a narrower profile than the 0.5 L reactor (IH/ID: 2.3). Syngas takes longer to pass through the catalyst slurry in a narrow reactor. A large commercial plant usually uses a slurry bubble column reactor without a stirrer to cut the equipment cost. The bubble column reactor has a very large IH to ID ratio to increase the CO conversion.

The active species is zero valence Co\(^0\) in the F-T synthesis. The desirable supports incorporate high surface areas and large pore sizes for greater distribution of Co\(^0\) particles. Small Co\(_2\)O\(_3\) particles are difficult to reduce to active Co\(^0\), so Zr is used as a promoter to decrease the reduction temperature of Co\(_2\)O\(_3\) particles\(^3\). Commercial SiO\(_2\) supports cannot simultaneously have high surface area and large pore size due to the reduction of pore size with higher surface area. Mesoporous silicas (MCM-41, HMS, SBA-15, FSM-16, and others) are important as supports for Co catalysts because of their combined high surface area and large pores\(^{13,14}\).
Fig. 4 Mass Fractions of Each Alcohol among the Total Alcohol Products from the Synthesis of Mixed Alcohols from Syngas in a Fixed-bed Reactor over CsCu/CeO2 at 573 K under 3 MPa.

Fig. 5 Mass Fractions of Each Alcohol among the Total Alcohol Products from the Synthesis of Mixed Alcohols from Syngas in a Fixed-bed Reactor over CsCu/CeO2 at 573 K under 3 MPa.

2.3. Synthesis of Mixed Alcohols from Syngas

2.3.1. Synthesis of Mixed Alcohols over Cu-based Catalysts

The synthesis of methanol from syngas (Eq. (2)) over Cu-based catalysts has been commercialized on a huge scale. ZnO has been used as a support for Cu-based catalysts in industry. The active intermediates formed on Cu0 species are stabilized by Cu+ species, so both Cu0 species and Cu+ species are important in the synthesis of methanol. Consequently, SiO2 is not a good support because Cu+ species cannot be formed on Cu/SiO2. Cu/CeO2 shows high catalytic activity in methanol reactions due to the strong interaction between metal and support15)−19). CeO2 is reducible, so the redox equilibrium with Cu0 (Ce4+ + Cu0 ↔ Ce3+ + Cu+) exists in Cu/CeO2. Therefore, both Cu0 species and Cu+ species are stabilized in Cu/CeO2, which results in the high catalytic activity.

\[
\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH} \quad (2)
\]

Cu-based catalysts also form a small amount of C2 + alcohols during the methanol synthesis. Addition of Cs to Cu-based catalysts increases the amount of C2 + alcohols. CH2O* species are an intermediate in the reaction and CH2O* desorbs from Cu surface to form methanol. However, two CH2O* combine to form \( \text{C}_2\text{H}_5\text{O}^* \) species via a direct coupling reaction which involves a nucleophilic attack of formaldehyde by adsorbed formyl species. The Cs+ basic sites stabilize the required \( \text{C}_2\text{H}_5\text{O}^* \) species which is then hydrogenated to form \( \text{C}_2\text{H}_5\text{OH} \), or further reacts with other formyl species to form propanol, butanol, and so on. The author found that CsCu/CeO2 catalyst formed a larger amount of C2 + alcohols than CsCu/ZnO catalyst during methanol synthesis from syngas20),21).

Figure 4 shows the mass fractions of each alcohol among the total alcohol products from the synthesis of mixed alcohols from syngas in a fixed-bed reactor over CsCu/CeO2 at 573 K under 3 MPa. CO conversion and selectivity for each product are shown in the inset of Fig. 4. Small amounts of C2+ hydrocarbons and dimethyl ether (DME) were also formed as by-products in the reaction (not listed in the inset of Fig. 4). The height of each bar in Fig. 4 shows the percentage of each alcohol of the total of various alcohols formed in the reaction. The amounts of C7+ alcohols were very low because the sum of C1-C6 alcohols was close to 100%. Methanol was the dominant alcohol and isobutanol was the second most abundant alcohol in the products. The C1 → C2 step is the slowest of the C-C bond forming steps, which forms methanol is the main product. The standard heat of enthalpy and the Gibbs free energy of isobutanol are the lowest among the C1-C4 alcohols, isobutanol is thermodynamically favored compared with ethanol and propanol. Moreover, the \( \text{C}_3\text{H}_6\text{O}^* \) intermediates also form isobutanol by aldol-type condensation on the basic CeO2 support.

The CsCu/CeO2 catalyst achieved high selectivity for alcohols (over 80%). The circulating reaction system for methanol synthesis in industry can be used for the synthesis of mixed alcohols on CsCu/CeO2 to increase the CO conversion. Consequently, the CsCu/CeO2 catalyst has the potential to co-produce C2 + alcohols (especially isobutanol) with methanol in current methanol synthesis plants.

2.3.2. Synthesis of Mixed Alcohols over Mo-based Catalysts

Mo-based catalysts can convert syngas to mixed alcohols (Eq. (3)). MoS2 obtained by sulfuration of MoO3 is the active species. SiO2 is a common catalyst support for MoS2. Montmorillonite is a type of layered clay which usually contains Na+ ions in the interlayer region. Large \( \text{AlO}_x\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12} \)2+ cations can be pillared in the interlayer region to substitute Na+ ions. A type of \( \text{Al}_2\text{O}_3\text{Mont} \)-pillared montmorillonite (denoted as \( \text{Al}_2\text{O}_3\text{Mont} \)) is formed by calcining \( \text{AlO}_x\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12} \)-pillared montmorillonite at 673 K in air. The author found that KNiMoS2/\( \text{Al}_2\text{O}_3\text{Mont} \) was an effective catalyst in the synthesis of mixed alcohols from syngas22).

\[
n\text{CO} + 2n\text{H}_2 = \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O} \quad (3)
\]

Figure 5 shows the mass fraction of each alcohol among the total alcohol products from the synthesis of mixed alcohols from syngas in a fixed-bed reactor over KNiMoS2/\( \text{Al}_2\text{O}_3\text{Mont} \) at 553 K under 8 MPa. CO conversion and selectivity for each product are shown in the inset of Fig. 5. CO conversion was 51.8% and selectivity for alcohols was 50.5% over KNiMoS2/\( \text{Al}_2\text{O}_3\text{Mont} \).
The formation of C2H6 from CO dissociation react with the absorbed H species formed on Cu-based catalysts. KNiMoS2/Al2O3-Mont has the potential to produce C2 hydrocarbons from syngas. The selectivity for CO2 is high because both C2H4 and C2H6 are formed over Mo-based catalysts. During the reaction, the C* species formed from CO dissociation react with the absorbed H* to form CH linear species on Ni sites. Methane is formed by the direct hydrogenation of CH linear species. CH linear species also react with non-dissociated CO (absorbed on the MoS2 phase) to form C2H5* intermediate. The formed C2H5* species is hydrogenated to form ethanol or is dehydrated to form C2H4. This route includes both chain growth via CH linear* intermediates and chain growth via C2H5* intermediates. Even without Ni, MoS2 can catalyze the process of chain growth via C2H5* intermediates although the efficiency is low. Therefore, MoS2 is the main catalyst and Ni is the co-catalyst in the NiMoS2-based catalysts. Basic K+ ion is a promoter to stabilize C2H5O* intermediates.

The ratio of C2 + OH to MeOH in the products formed over Mo-based catalysts is much higher than that formed on Cu-based catalysts. KNiMoS2/Al2O3-Mont catalyst has the potential to produce C2 + alcohols from syngas. The selectivity for CO2 is high because MoS2 catalyzes the water-shift reaction (CO + H2O = CO2 + H2). This is not a serious problem because the formed CO2 can be converted to CO by the reverse water-shift reaction. Selectivity for hydrocarbons is high because CH linear* is an intermediate in the reaction system. However, the high reaction pressure required is a disadvantage for the commercial application of MoS2-based catalysts in mixed alcohol synthesis.

Mo loading: 15 wt%; Ni loading: 3.0 wt%; K loading: 1.0 wt%. Input gas: 30 % CO + 60 % H2 + 10 % N2; GHSV: 2400 h-1.

Fig. 5  Mass Fraction of Each Alcohol among the Total Alcohol Products from the Reaction of Mixed Alcohols from Syngas in a Fixed-bed Reactor over KNiMoS2/Al2O3-Mont at 553 K under 8 MPa

| Catalyst          | CO conv. [%] | Selectivity [%] | EtOH/MeOH |
|-------------------|--------------|-----------------|-----------|
| Rh/SiO2           | 10.1         | 42.4            | 55.4      | 2.2 | 4.91 |
| Rh/ZrO2           | 18.2         | 39.5            | 58.0      | 2.5 | 8.26 |
| Rh/MgO            | 10.8         | 60.7            | 37.4      | 1.9 | 0.58 |
| Rh/Co3             | 23.7         | 48.8            | 35.9      | 15.3 | 1.66 |
| Rh/Co3/ZrO2        | 27.3         | 52.1            | 27.8      | 10.1 | 4.46 |

a) Catalyst amount: 1 g; Rh loading: 2 wt%; W/F: 10 g h mol-1; input gas: 30 % CO + 60 % H2 + 10 % N2.
b) Oxygenates, including MeOH, EtOH, C3 + OH, CH3CHO, CH3COOC2H5, CH3COOCH3, C2H5OC2H5, CH3COOH, and so on.
c) Hydrocarbons, mainly CH4.
d) Mass ratio of EtOH to MeOH.

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2.4. Synthesis of Ethanol from Syngas

2.4.1. Direct Synthesis of Ethanol from Syngas over Rh-based Catalysts

Rh-based catalysts can convert syngas to C2-oxygenates, especially ethanol (Eq. 4)). SiO2 is a common support for Rh catalysts. (Rh0, Rh+, Rh2+)O-M is the active site for the formation of C2-oxygenates. Therefore, both Rh0 species and Rh+ species are important in the synthesis of ethanol. Consequently, supports with strong interactions with Rh are suitable for the reaction. The author found that CeO2 and TiO2 are effective supports for Rh catalysts in the synthesis of ethanol from syngas.

Table 2 lists the results of synthesis of C2-oxygenates from syngas in a fixed-bed reactor over Rh-based catalysts at 548 K under 2.4 MPa. Rh/Co3 achieved much higher CO conversion than Rh/SiO2, Rh/MgO, and Rh/ZrO2. Moreover, CO conversion over Rh/Co3/ZeO2 was higher than that over Rh/Co3. Doping of Zr+4 ions in the cubic structure of CeO2 decreased the crystallization degree of CeO2, which resulted in higher BET surface area. Moreover, Rh+ active species became more stable in Rh/Co3/ZeO2 because doping of Zr+4 ions in CeO2 improved the reducibility of the support. Rh supported on basic MgO showed a low EtOH/MeOH ratio. Rh supported on acidic ZrO2 showed a high EtOH/MeOH ratio but the selectivity for hydrocarbons was high.

Figure 6 shows the reaction route for the formation of C2-oxygenates from syngas over Rh-based catalysts. Activity for cleaving the C = O bond of adsorbed CO* greatly influences the product. Cu cannot cleave the
C = O bond and forms CH$_3$OH through the CH$_2$O* intermediate. Ni, Fe, Co, and Ru cleave all CO* to form (CH$_2$)$_n$ intermediates, so that no CO* is present in the system and thus all (CH$_2$)$_n$ are converted to hydrocarbons. Rh can cleave some CO* and the remaining CO* reacts with (CH$_2$)$_n$ to form C$_2$-oxygenates. Acidic supports promote the dehydration of CH$_2$O* to form (CH$_2$)$_n$ intermediates, which increases the concentration of (CH$_2$)$_n$ intermediates and thus increases the selectivity for C$_2$-oxygenates and CH$_4$. In contrast, basic supports inhibit the dehydration process from CH$_2$O* to (CH$_2$)$_n$, which increases the concentration of CH$_2$O* and thus increases the selectivity for methanol.

Rh/Ce$_{0.8}$Zr$_{0.2}$O$_2$ has the potential to produce ethanol from syngas because all C$_2$-oxygenates can be reduced to ethanol in H$_2$. Selectivity for CH$_4$ is relatively high (about 30 %) because (CH$_2$)$_n$ is the common intermediate to form C$_2$-oxygenates and CH$_4$. However, the high price of Rh is a disadvantage for the commercial application of Rh-based catalysts to ethanol synthesis from syngas.

2.4.2. Indirect Synthesis of Ethanol through the Three-step Process

CH$_4$ formation in the direct synthesis of ethanol is difficult to suppress because (CH$_2$)$_n$ is the common intermediate to form ethanol and CH$_4$. The author designed an indirect three-step process for the synthesis of ethanol from syngas using methanol as a carrier$^{26}$. Methanol has been used as a carrier in propylene epoxidation by molecular oxygen$^{27-31}$.

Figure 7 shows the indirect method for ethanol synthesis from syngas using methanol as a carrier. DME carbonylation (Eq. (6)) is a slow reaction so a novel catalyst containing Rh and heteropolyacid was developed for DME carbonylation$^{32}$. However, a high CO/DME ratio of 50 was still used in the DME carbonylation to increase DME conversion$^{36}$. The indirect process will further also require the development of active catalyst for DME carbonylation and design of an effective system to recycle the excess CO reactant in the DME carbonylation.

In general, selectivity is more important than conversion for a catalyst used in industrial production. The conversion can be improved by the chemical process technology. Industrial production of methanol from syngas is carried out in a circulating flow system to increase the CO conversion which is limited by the reaction equilibrium. The selectivity is difficult to improve by process technology because the selectivity is decided by the catalyst characteristics. Direct synthesis of ethanol over Rh-based catalysts has been investigated for over thirty years, but has not been commercialized because the amount of by-product CH$_4$ cannot be suppressed. The indirect method can obtain high selectivity for ethanol although the process is complicated. The indirect method has greater potential for the industrial production of ethanol because the process efficiency can be improved by process technology. Other indirect methods for ethanol synthesis are likely to be developed in the future.

3. Catalytic Reactions in the Hydrotreatment Process

Hydrotreatment is an important industrial process to produce hydrocarbon biofuels. The hydrotreatment process includes hydroisomerization, hydrocracking, and hydrodeoxygenation. Bifunctional catalysts containing metal and solid acid are used in the hydrotreatment process. The balance between metal and solid acid is important for the product distribution.

3.1. Upgrading of F-T Gasoline

The F-T synthesis produces mixed n-paraffins, which mainly consist of normal C5-C9 gasoline-range hydro-

\[
\text{CH}_3\text{COOCH}_3 + 2\text{H}_2 = \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{OH} \quad (7)
\]

Each reaction in Eqs. (5)-(7) can be achieved with high selectivity, so the selectivity for ethanol of the indirect process can be maintained at over 90 % under 1 MPa$^{30}$. DME carbonylation (Eq. (6)) is a slow reaction so a novel catalyst containing Rh and heteropolyacid was developed for DME carbonylation$^{32}$. However, a high CO/DME ratio of 50 was still used in the DME carbonylation to increase DME conversion$^{36}$. The indirect process will further also require the development of active catalyst for DME carbonylation and design of an effective system to recycle the excess CO reactant in the DME carbonylation.

![Figure 6 Reaction Route for the Formation of C2-oxygenates from Syngas Over Rh-based Catalysts](image1)

![Figure 7 Indirect Method for Ethanol Synthesis from Syngas Using Methanol as a Carrier](image2)
Table 3 Results of Upgrading of F-T Gasoline in a Fixed-bed Reactor at 523 K under Normal Pressure

| Catalyst | Time on stream | Mass ratio of iso/n | Lumped composition [%] |
|----------|----------------|---------------------|------------------------|
|          |                | C1-C4 | C5-C9 | C10 + |
| Feed stock | 0.05 | 0.8 | 74.0 | 25.2 |
| Pt/Al2O3 | 5 min | 0.11 | 1.6 | 74.6 | 23.8 |
|          | 5 h  | 0.09 | 1.3 | 74.3 | 24.4 |
| Cs2.5H0.5PW12O40 | 5 min | 5.33 | 8.8 | 87.3 | 3.9 |
|          | 5 h  | 0.42 | 2.6 | 76.9 | 20.5 |
| Pt/Al2O3 + Cs2.5 | 5 min | 8.67 | 4.5 | 94.5 | 1.0 |
|          | 5 h  | 8.45 | 4.4 | 94.4 | 1.2 |

a) Catalyst amount: 1 g; LHSV: 20 h⁻¹; H2 feed stock: 200 mL/mL.
b) Pt loading: 1 wt%.c) Mass ratio of 1 wt% Pt/Al2O3 to Cs2.5H0.5PW12O40: 1/1; co-grinding time: 20 min.

Adapted from ref. 33. Copyright (2011) ELSEVIER.

carbons (called F-T gasoline). F-T gasoline was collected in the cold trap set behind the slurry reactors (Fig. 3). However, the octane number of n-paraffins is very low, so upgrading of F-T gasoline to increase the amount of high octane number iso-paraffins is important in industry. Heteropolyacids are excellent solid acid catalysts in both gas-solid and liquid-solid reaction systems. H3PW12O40 is the strongest heteropolyacid. Cs2.5H0.5PW12O40 (Cs2.5), an acidic salt of H3PW12O40, has a similar acid strength to H3PW12O40 but its surface area is much larger than that of H3PW12O40. The author found that bifunctional catalyst containing Pt and Cs2.5 is an excellent catalyst for the upgrading of F-T gasoline.

Table 3 shows the results of upgrading of F-T gasoline in a fixed-bed reactor at 523 K under normal pressure. The F-T gasoline feedstock (obtained from the trap behind 12.5 L slurry reactor) contained 25.2 wt% C10 + hydrocarbons with a very low ratio of iso/n (0.05). Therefore, upgrading of F-T gasoline requires two modifications: isomerization of C5-C9 n-paraffins and cracking of C10 + hydrocarbons. The activity of Pt/Al2O3 was very low due to the low iso/n ratio in product. The iso/n ratio over Cs2.5 was 5.33 after 5 min on stream but decreased to 0.42 after 5 h on stream. Therefore, Cs2.5 was severely deactivated during the reaction. The catalyst containing Pt/Al2O3 and Cs2.5 formed a large amount of C5-C9 with high iso/n ratio even after 5 h on stream. Consequently, the synergy effect of Pt and Cs2.5 is important in the upgrading of F-T gasoline.

Figure 8 shows the reaction mechanisms involved in the upgrading of F-T gasoline. Carbenium ion is the key intermediate in the hydroisomerization of n-paraffins. Reaction on a solid acid catalyst forms the initial carbenium ions from n-paraffins through hydride elimination or proton addition followed by hydrogen elimination, which represents an acid-catalyzed mono-functional mechanism. Addition of Pt to the solid acid catalyst allows rapid formation of n-olefins by the dehydrogenation of n-paraffins. The formed n-olefins are protonated on the solid acid sites to form carbenium ions. This bifunctional mechanism involves hydrogenation-dehydrogenation on the Pt sites and isomerization on the solid acid sites. The reaction rate through the bifunctional mechanism is fast because the n-carbenium ions are easily formed by the H⁺ addition to olefin. The carbonaceous deposit ( coke) formed on the acid sites (by polymerization of carbenium ions) causes deactivation of the solid acid catalyst. Introduction of Pt to the solid acid can reduce such deactivation by hydrogenation of the coke precursor with H2. Cracking is a competitive reaction with isomerization due to the common carbenium ion intermediate. Cracking of a large carbenium ion forms a light carbenium ion and an olefin through β-scission. The relative reactivity of n-paraffins to hydrocracking greatly increases with higher carbon number of the paraffin. Consequently, n-C11-H26 underwent isomerization without cracking, but n-C8-H14 underwent isomerization without cracking over the Pt/Al2O3 + Cs2.5 catalyst.

3.2 Hydrocracking of F-T Waxes

The product of F-T synthesis contains a large fraction of heavy hydrocarbons due to the chain growth mechanism. The formed C20+ hydrocarbons are called F-T waxes because they solidify at room temperature. Therefore, hydrocracking of F-T waxes is an important process to increase the yield of liquid fuels in the F-T synthesis. The author selectively hydrocracked F-T waxes to form diesel-range and gasoline-range hydrocarbons using bifunctional catalysts containing metal and solid acid.

Figure 9 shows FID-GC charts of various samples from the hydrocracking of F-T waxes. The F-T waxes obtained from the distillation of F-T products are a mixture containing a large fraction of long-chain n-paraffins with small fractions of n-olefins and iso-paraffins. The liquid product obtained from the hydrocracking of F-T waxes over Pt/Al13-Mont contained a large fraction of C11-C20 hydrocarbons with a high n/iso ratio. This product can be used as a high-quality diesel fuel with a high cetane number. The liquid product obtained from
the hydrocracking of F-T waxes over Pt/H-Y contained a large fraction of C5-C10 hydrocarbons with a low n/iso ratio. This product can be used as a high-quality gasoline with a high octane number.

Figure 10 shows the schematic illustration for the hydrocracking of F-T waxes over bifunctional catalysts containing Pt and solid acid. Carbenium ion is a key intermediate in the hydrocracking of n-paraffins. Carbenium ions in the middle of the carbon chain are more stable than those at the end of the carbon chain. Consequently, cracking of hydrocarbons preferentially occurs in the middle of the carbon chain. The relative reactivity of large hydrocarbons for hydrocracking greatly increases with higher carbon number. A long carbon-chain hydrocarbon is easily cracked whereas a short carbon-chain hydrocarbon is difficult to crack in the reaction system. Therefore, the products from the hydrocracking of F-T waxes can be controlled by using various solid acid catalysts; the solid wax C26H66 is cracked to C16H34 (diesel-range) on weak solid acid (such as Al13-Mont); the formed C16H34 is further cracked to C8H18 (gasoline-range) on medium strong solid acid (such as H-Y); and the formed C8H18 is further cracked to C4H10 (LPG) on strong solid acid (such as H-ZSM-5).

3.3 Hydrotreatment of Vegetable Oils

Vegetable oils are not suitable for direct utilization in current diesel engines due to their high viscosity. Therefore, conversion of vegetable oils to biodiesel is important in the development of biofuels. Fatty acid methyl ester (FAME) produced by transesterification of vegetable oil with methanol is the first generation of biodiesel. FAME has some disadvantages as a transportation fuel because the molecules contain both C–C bonds and C–O bonds. Bio-hydrogenated diesel (BHD) produced from the hydrotreatment of vegetable oil is the next generation of biodiesel. Mixed paraffins can be obtained after all C=C double bonds have been hydrogenated and all oxygen atoms have been eliminated by the hydrotreatment process.

The main components of vegetable oils are triglycerides and fatty acids with carbon chains containing 16 carbons and 18 carbons. Deoxygenation of C17H35COOH (stearic acid, containing 18 carbons in the carbon chain) involves three parallel reactions: reduction (Eq. (8)), decarbonylation (Eq. (9)), and decarboxylation (Eq. (10)). Using a fatty acid with an even number of carbons, reduction produces a normal paraffin with an even number of carbons plus water; decarbonylation produces a normal paraffin with an odd number of carbons plus water and CO; and decarboxylation produces a normal paraffin with an odd number of carbons plus CO2.

Table 4 shows the results of hydrotreatment of vegetable oils in a fixed-bed reactor over NiMo/SiO2-Al2O3 at 623 K under 4 MPa H2. The yield of BHD was over 80% and the yield of LPG was around 5% from various vegetable oils. During the reaction, the C=C double bonds are quickly saturated, and the fatty acids and triglycerides are deoxygenated at the same time. Consequently, vegetable oils with various degrees of acidity and various degrees of unsaturation can be converted to BHD and LPG in the one-step process.
SiO$_2$–Al$_2$O$_3$ had similar physical and chemical properties (iso/n ratio, pour point, density, and viscosity).

**Figure 11** shows the chemistry of the hydrotreatment of vegetable oils over catalysts containing metal and solid acid. The metal sites catalyze hydrogenation and deoxygenation to convert vegetable oil to C$_3$H$_6$ and C$_{15}$-C$_{18}$ n-paraffins. The solid acid sites catalyze hydroisomerization and hydrocracking of C$_{15}$-C$_{18}$ n-paraffins to decrease the viscosity of BHD. Both noble catalysts (Ru, Pt, Pd, etc.) and MoS$_2$-based catalysts (sulfided Ni-Mo, sulfided Co-Mo, etc.) had deoxygenation activity to produce BHD from vegetable oils$^{42)\text{--}48)$. The noble catalysts are suitable for feedstocks not containing sulfur compounds because sulfur causes deactivation of the noble catalysts. The MoS$_2$-based catalysts are suitable for feedstocks containing sulfur compounds which supplement the loss of sulfur from the catalyst surface during the reaction.

### 4. Conversion of Algae Oils to Jet Fuel

Hydrocarbon bio-jet fuel can be produced by the BTL process (including F-T synthesis and F-T wax hydrocracking) and the hydrotreatment of vegetable oils. Recently, algae oils have attracted much attention worldwide because the oil yields from algae are significantly higher than those from any other crop. Algae-to-jet fuel (ATJ) is becoming an important process in the production of biofuels. Large-scale cultivation of oil-produced algae is the key technology for the utilization of algae oils. The oil-producing algae *Botryococcus* and Euglena have been cultivated outside the laboratory. Various algae produce oils with various chemical compositions. *Botryococcus* oil is a mixture of large hydrocarbons and Euglena oil is a mixture of saturated esters.

#### 4.1. Hydrocracking of *Botryococcus* Oil

**Figure 12** shows the molecular structures of *Botryococcus* oil (Bot-oil) and squalene. Squalene (C$_{30}$H$_{50}$) is a model compound for Bot-oil. Bot-oil consists of large hydrocarbons with the formula of C$_n$H$_{2n}$–10 ($n =$ 29–34). The $n$ value (from 29 to 34) is decided by the number of methyl branches (broken line in **Fig. 12**). Bot-oil and squalene both contain six C=C double bonds in one molecule. Bot-oil is very suitable as a precursor for jet fuel because it contains multi-branch hydrocarbons with low freezing points. The author investigated the hydrocracking of Bot-oil using Ni-Mo-based and Pt-Re-based catalysts$^{49),50)$. **Figure 13** shows FID-GC charts of Bot-oil and liquid product after reaction over NiMo/Al$_2$O$_3$-Mont at 573 K for 6 h. The Bot-oil feedstock contained i-C$_{30}$H$_{50}$ as the main component (90 %) with some other hydrocarbons and fatty acids. After reaction, all peaks in the liquid product were saturated hydrocarbons because fatty acids were deoxygenated to paraffins and olefins were hydrogenated to paraffins under the H$_2$ atmosphere$^{49),50)$. The yield of C$_{10}$-C$_{15}$ jet-fuel-range hydrocarbons was 51.2 % and the yield of C$_5$-C$_9$ gasoline-range hydrocarbons was 32.8 %. During the reaction, the C=C double bonds in the molecules of Bot-oil were quickly hydrogenated to form saturated hydrocarbons on the catalyst metal sites. Then, the saturated hydrocarbons were cracked on the solid acid sites. Cracking in the middle of the carbon chain is easier than cracking at the end of the carbon chain over bifunctional catalysts. A long carbon-chain hydrocarbon is easier to crack than a short carbon-chain hydrocarbon. A weak acid cannot but a strong acid can crack a short carbon-chain hydrocarbon. Therefore, Bot-oil

### Table 4 Results of Hydrotreatment of Vegetable Oils in a Fixed-bed Reactor over NiMo/SiO$_2$–Al$_2$O$_3$ at 623 K under 4 MPa H$_2$

| Oil     | BHD [%] | LPG | CO$_2$ [%] | H$_2$O [%] |
|---------|---------|-----|------------|------------|
| Jatropha| 83.5    | 4.9 | 2.4        | 8.9        |
| Canola  | 81.4    | 5.7 | 2.1        | 9.5        |
| Palm    | 82.1    | 5.4 | 2.3        | 9.3        |

a) Catalyst amount: 1 g; Mo loading: 15 wt%; Ni loading: 3.0 wt%; LHSV: 7.6 h$^{-1}$; H$_2$/oil ratio in feed: 800 mL/mL.

Adapted from ref. 43. Copyright (2011) American Chemical Society.

![Fig. 11 Chemistry of the Hydrotreatment of Vegetable Oils over Catalysts Containing Metal and Solid Acid](image1)

![Fig. 12 Molecular Structures of Bot-oil and Squalene](image2)

![Fig. 13 FID-GC charts of Bot-oil and liquid product after reaction over NiMo/Al$_2$O$_3$-Mont at 573 K for 6 h](image3)

J. Jpn. Petrol. Inst., Vol. 64, No. 6, 2021
was cracked to jet fuel-range hydrocarbons on the weak solid acid sites, and further cracked to gasoline-range hydrocarbons on the relatively strong solid acid sites.

4.2. Deoxygenation of Euglena Oil

Euglena oil is a mixture of saturated esters with long carbon chains \(C_mH_{2m+1}COOC_{n}H_{2n+1}\), \(m = 11-15, n = 12-16\). Hexadecyl palmitate \((C_{15}H_{31}COOC_{16}H_{33})\) was used as a model compound for Euglena oil. The author investigated the deoxygenation of \(C_{15}H_{31}COOC_{16}H_{33}\) under \(H_2\) and \(N_2\) atmospheres using the Pd/Mg(Al)O catalyst derived from Pd-containing MgAl-type hydro-talcite\(^{51}\).

Figure 14 shows the FID-GC charts of \(C_{15}H_{31}COOC_{16}H_{33}\), liquid product after reaction in \(H_2\), and liquid product after reaction in \(N_2\). The products from the deoxygenation of \(C_{15}H_{31}COOC_{16}H_{33}\) in \(H_2\) were \(n-C_{16}H_{34}\) and \(n-C_{15}H_{32}\). The molar ratio of \(n-C_{16}H_{34}\) to \(n-C_{15}H_{32}\) was 4.3. The deoxygenation of \(C_{15}H_{31}COOC_{16}H_{33}\) under \(H_2\) atmosphere involves three parallel reactions: reduction (Eq. (11)), decarbonylation (Eq. (12)), and decarboxylation (Eq. (13)). Reduction of one \(C_{15}H_{31}COOC_{16}H_{33}\) molecule forms two \(C_{16}H_{34}\) molecules. Either decarbonylation or decarboxylation of one \(C_{15}H_{31}COOC_{16}H_{33}\) molecule forms one \(C_{16}H_{34}\) molecule and one \(C_{15}H_{32}\) molecule. Reduction of \(C_{15}H_{31}COOC_{16}H_{33}\) was the main reaction because the amount of \(n-C_{16}H_{34}\) greatly exceeded that of \(n-C_{15}H_{32}\) in the product.

\[
\begin{align*}
C_{15}H_{31}COOC_{16}H_{33} + 4H_2 &= 2C_{16}H_{34} + 2H_2O \quad (11) \\
C_{15}H_{31}COOC_{16}H_{33} + 2H_2 &= C_{15}H_{32} + C_{16}H_{34} + CO + H_2O \quad (12) \\
C_{15}H_{31}COOC_{16}H_{33} + H_2 &= C_{15}H_{32} + C_{16}H_{34} + CO_2 \quad (13)
\end{align*}
\]

The decarboxylation reactions (Eqs. (14), (15)) occurred in the deoxygenation of \(C_{15}H_{31}COOC_{16}H_{33}\) under \(N_2\). The number of H atoms in the \(C_{15}H_{31}COOC_{16}H_{33}\) molecule is not adequate to obtain saturated \(C_{16}H_{34}\) and \(C_{15}H_{32}\) without supply of more \(H_2\), so one \(C_{15}H_{31}COOC_{16}H_{33}\) molecule forms one paraffin and one olefin by decarboxylation under the \(N_2\) atmosphere. The amount of \(1-C_{16}H_{32}\) was much larger than that of \(1-C_{15}H_{30}\) in the product, indicating that Eq. (14) was the main reaction in the deoxygenation of \(C_{15}H_{31}COOC_{16}H_{33}\) under \(N_2\). A few heavy hydrocarbons larger than \(C_{16}\) were formed by olefin polymerization and some \(C_{10}-C_{14}\) hydrocarbons were formed by the cracking of these large olefins.

\[
\begin{align*}
C_{15}H_{31}COOC_{16}H_{33} &= C_{15}H_{32} + C_{16}H_{32} + CO_2 \quad (14) \\
C_{15}H_{31}COOC_{16}H_{33} &= C_{15}H_{30} + C_{16}H_{34} + CO_2 \quad (15)
\end{align*}
\]

Hydrotreatment of Euglena oil over Pd/Mg(Al)O
under H₂ formed a mixture of normal C10-C16 hydrocarbons but the freezing point of the product was high. Using an acidic support for Pd can decrease the freezing point of the product (by isomerization) but the yield of jet fuel-range hydrocarbons was reduced due to hydrocracking. However, deoxygenation of Euglena oil containing Ni and solid acid. Ethylene oligomerization over bifunctional catalysts containing Ni and solid acid. Ethylene oligomerization over Ni is an A-S-F type polymerization. The products obey a A-S-F distribution in the order of C₄ > C₆ > C₈ > C₁₀. The acid sites catalyze the reaction by forming carbenium ions which undergo cracking, isomerization, and dimerization in the reaction system. H-ZSM-5 is a strong solid acid and cracked almost all C₆ + products in the reaction system. Ni/H-ZSM-5 formed C₈H₁₆ from both the reaction of C₆H₁₂ with C₂H₄ (on Ni sites) and the dimerization of C₆H₆ (on acid sites). The textural porosity of Al-HMS improved the selectivity for C₆H₁₆ compared to Ni/AI-HMS.

The author designed a reaction system contained two fixed-bed reactors and one cold trap to link ethanol dehydration and ethylene oligomerization in the one-step system. The cold trap was used to eliminate steam from the mixed gas before the second step of ethylene oligomerization. After feeding ethanol to the reaction system for 1 h, the yields of C₂H₄, C₃H₆, C₆H₁₂, C₈H₁₆, and C₈ + were maintained at 1.8, 35.7, 22.5, 22.1, and 7.6 %, respectively.

The product from the ethylene oligomerization on Ni/H-ZSM-5 can be used as LPG fuel after hydrogenation. Ni/AI-HMS forms a large amount of C₆-C₈ olefins, which can be converted to gasoline by hydrogenation. C₆-C₈ olefins also can be converted to jet-fuel range hydrocarbons through an extra dimerization process. Moreover, conversion of n-butanol (obtained from acetone–butanol–ethanol fermentation) and isobutanol (synthesized from syngas) are expected to produce jet-fuel-range hydrocarbons in the one-step oligomerization of butene.

### 5.2 Hydrocracking of Polyethylene

Polyethylene has been produced on the industrial scale from ethylene polymerization by the Ziegler-Natta catalytic process. Bio-polyethylene can be obtained from bioethanol using the current industrial process, so
hydrocracking of polyethylene to jet fuel-range hydrocarbons is an important reaction in the ETJ process. The author developed bifunctional catalysts containing Pt and Al-modified MCM-48 for the hydrocracking of polyethylene to jet fuel-range hydrocarbons\(^5\)\(^5\).

**Figure 16** shows the GC-MS chromatogram of the liquid product from hydrocracking of polyethylene over Pt/Al/MCM-48. The liquid product obtained from the hydrocracking of polyethylene on Pt/Al/MCM-48 contained many hydrocarbons with carbon numbers ranging from 6 to 19. Paraffins were the major components, whereas olefins and aromatics were present in very low amounts in the product. C\(_{11}\) and C\(_{12}\) hydrocarbons were the largest components in the GC-MS chromatogram. C\(_{9}\)-C\(_{15}\) jet fuel-range hydrocarbons accounted for a large fraction of the product.

Polyethylene molecules are cracked through chain-end scission and random scission. Chain-end scission of polyethylene forms CH\(_4\), C\(_2\)H\(_6\), and long-chain hydrocarbons. The formed long-chain hydrocarbons subsequently undergo further cracking by chain-end scission. Hydrogenolysis of polyethylene on metal catalysts (without solid acid) undergo chain-end scission to form large amounts of CH\(_4\) and C\(_2\)H\(_6\). On the other hand, random scission is accelerated by introducing acid sites to achieve hydrocracking through carbenium ion intermediates. The carbenium ions prefer to form in the middle of carbon chains and crack through \(\beta\)-scission. Catalysts containing Pt and H-Y (a relatively strong acid) formed a large amount of gasoline-range hydrocarbons. Pt/Al/MCM-48 catalyst achieved a high yield of jet fuel-range hydrocarbons because Al/MCM-48 has suitable weak acidity and cubic mesopore structure.

6. **Summary**

All types of biomass (woody biomass, waste biomass, etc.) can be converted to liquid hydrocarbon fuels by the BTL process through the syngas platform. Vegetable oils and algal oils can be converted to liquid hydrocarbon fuels by the hydrotreatment process. Bioethanol can be converted to liquid hydrocarbon fuels through ethylene oligomerization or polyethylene hydrocracking. All catalytic reactions can be divided into three groups by comparing the carbon numbers of the reactant and product: carbon-number increasing reactions (F-T synthesis, mixed alcohols synthesis, C\(_2\)H\(_4\) oligomerization), carbon-number constant reactions (isomerization, deoxygenation), and carbon-number decreasing reactions (cracking). Carbon-number increasing reactions unavoidably form various carbon-number products by obeying the A-S-F distribution. Solid acid catalysts are necessary for isomerization and metal catalysts are necessary for deoxygenation. Bifunctional catalysts containing metal and solid acid are suitable for hydrocracking. Large hydrocarbons can be selectively hydrocracked to various light distillate hydrocarbons by adjusting the solid acidity in the bifunctional catalysts.

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要　　旨
各種バイオマス原料から液体輸送燃料への触媒変換

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著者の研究に基づいて、本総合論文は各種バイオマス原料から液体輸送燃料を製造する化学プロセスに含まれる触媒反応を紹介した。特に、バイオ炭化水素系液体燃料の製造に重点を置いた。今回、取り上げた化学プロセスは、（1）バイオ合成ガスの炭化水素およびアルコールへの変換、（2）植物油の炭化水素への変換、（3）藻類生産油の炭化水素への変換、（4）バイオエタノールの炭化水素への転換の4種類である。本論文の触媒技術は、これらの化学プロセスを成り立たせる、重合あるいは水素化処理である。重合反応系としてはフィッシャー－トロプシュ合成、混合アルコールの合成およびエチレンのオリゴマー化が含まれ、水素化処理反応系としてはクラッキング、異性化、脱酸素が属しており、それぞれの反応に適する金属触媒、固体酸触媒あるいは金属と固体酸を含む二元機能触媒を開発した。
なお触媒の開発で、各種触媒反応の特性に応じて、スラリー式反応器、固定床流通式反応器あるいはオートクレープパッチ式反応器を用いて検討した。さらに、これらの触媒開発において、活性金属種、担体効果および二元機能触媒における金属と固体酸のバランスについて検討した。これらの触媒およびプロセス開発を通じて、各種バイオマス原料を従来石油由来のガソリン、軽油、LPG燃料、およびジェット燃料と同等の化学組成を有する炭化水素系バイオ燃料に変換するルートを確立することができた。

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