In order to utilize biomass as new resources of petrochemicals, catalytic conversion of oxygen-containing intermediates which can be derived from biomass was investigated. By using ZSM-5 as the catalyst, ethylmethylketone was converted to aromatic and aliphatic hydrocarbons at high yields. Selectivity for aromatics was found 70 – 80 %, and the major components were xylene and toluene. Selectivity for aliphatics was about 25 %, and the major components were olefins such as propylene, butene and ethylene. The formation of CO2 and CO was only 2 – 3 %. When acetone, acetaldehyde, propionaldehyde, levulinic acid were used as the feed materials, similar results were obtained.

Keywords: chemicals from biomass, catalytic conversion, ZSM-5, biorefinery.

1. Introduction

The significance of biomass conversion to fuel oil or chemicals has become widely recognized as one of the renewable resources which can be alternatively used in place of petroleum under the circumstance of rising crude oil price. Utilization of biomass also serves to reduce the dependency on fossil resources and lower CO2 emission. For this purpose, many attempts of biomass conversion such as flash pyrolysis, decomposition under hydrothermal conditions, fermentation, etc., have been made to obtain fuel oil equivalent products.

However, in the conversion of biomass into fuel oil equivalent products, there remain problems such as small price difference between the product and biomass and the low grade properties of the products compared to conventional petroleum oils due to oxygen-containing components. For example, bio oil produced by flash pyrolysis or products of hydrothermal reaction contains a large amount of the oxygen-containing components such as organic acids, ketones and aldehydes.

By hydrothermal conversion of saccharides under near critical condition of water with or without acids or bases, glycolaldehyde, glyceraldehyde, dihydroxyacetone, 5-hydroxymethylfurfural (5-HMF) and furfural can be obtained [1]. From a recent research by the authors [2, 3], bagasse or erianthus could be converted to levulinic acid at a high yield in the hydrothermal reaction with acid catalyst. Levulinic acid can be converted to hydroxy-ethylmethylketone, and hydroxy-ethylmethylketone can be easily converted to ethylmethylketone (EMK) by catalytic reaction under hydrogen atmosphere. Masuda et al. [4] reported that acetone and EMK containing liquid could be obtained from palm shell oil by catalytic reaction with FeOOH/ZrO under hydrothermal condition.

Bio oil produced by the flash pyrolysis of wood contains many oxygen-containing compounds, for example, acids and aldehydes such as acetic acid and glycolaldehyde [5-7]. The oxygen-containing compounds exist as a mixture in the bio oil and it is difficult to separate them at a low cost.

Therefore, in order to upgrade bio oil or hydrothermally treated liquid to products with higher value and better utilizability, it is considered very important to convert these oxygen-containing intermediates in the mixture into hydrocarbon chemicals of higher value. The product hydrocarbons can be used as basic raw materials of petrochemical industry. Recently, the concerns about the biomass-derived hydrocarbons are growing for synthesizing environmentally benign polymers.

For this purpose, the conversion of acetone into benzene, toluene, xylene, as a model reaction, with ZSM-5 was investigated and the result was reported [8]. In this paper, the conversion of various oxygen-containing compounds such as ethylmethylketone (EMK), levulinic acid, aldehydes with ZSM-5 is investigated.

2. Experimental

2.1. Catalyst And Feed Materials

As the catalyst, ZSM-5 (proton type) with Si/Al=25 in the form of pellet was used. As feed materials, ethylmethylketone, acetone,
acetaldehyde, propionaldehyde, levulinic acid were used.

2.2. Reaction Apparatus

Fig. 1 shows the reaction system used in this work. A fixed bed reactor made of SUS-316 tube with 6 mm inner diameter and 600 mm length was used and installed in an electric furnace. 1 g of ZSM-5 powder was mixed with 5 g of inactive quartz sand (10-15 mesh) and packed in the constant temperature zone of 200 mm length. At the inlet of the reactor, a pre-heating zone was installed where a temperature lower than the reactor temperature by 50 K was maintained.

Figure 1: Experimental system

Feed material was supplied to the pre-heating zone by a double plunger pump or a syringe pump and mixed with nitrogen carrier gas. In the case of levulinic acid, hydrogen gas was used instead of nitrogen. Flow rate of the carrier gas was 30-35 standard ml/min.

At the outlet of the reactor, an air-cooling column with 4 mm inner diameter and 100 mm length was connected, and, next to it, two cold traps cooled at 273 K in an water bath with ice, in series, were equipped. In this recovery system, product oils and unconverted feed material were recovered. The carrier gas containing product gas was collected by a gas bag.

2.3. Analysis Of The Product

The recovered oil in the cold traps was analyzed by a gas chromatograph (Hewlett-Packard 5890) equipped with a FID detector and a DB-1 capillary column (60 m). The gas was analyzed by two gas chromatographs (Shimadzu GC-8A) with TCD detectors, one equipped with Molecular sieve 13X and the other with Porapak-Q packed column, respectively.

2.4. Reaction Conditions

After the reactor temperature reached the reaction temperature, the temperature was maintained for an hour with carrier gas stream, then, the feed material was introduced. The reaction was conducted under nitrogen or hydrogen atmosphere at normal pressure. The reaction temperature was 673 K for aldehydes and ketones, and, in the experiment of levulinic acid, the reaction temperature was varied in the range of 673-823 K to investigate the effect of temperature. The contact time of the reactant with the catalyst was 6-7.5 s for the mixture of ZSM-5 and quartz sand which corresponded to 2-2.5 s for ZSM-5. The space velocity of liquid feed material to the catalyst (ZSM-5) was 4 g/(g h) for aldehydes and ketones, 1 g/(g h) for levulinic acid.

3. Results And Discussion

3.1. Conversion Of Methylethylketone (MEK)

Using ethylmethylketone as a feedstock, reaction over ZSM-5 was carried out at 673 K for 10 hours, and conversion of feedstock and product selectivity were investigated. The conversion X is defined as

\[ X = \left(1 - \frac{F}{F_0}\right) \times 100 \]

where F and F₀ are molar quantity of ethylmethylketone in the product and in the feed, respectively. The selectivity \(S_i\) is defined as

\[ S_i = \left(\frac{C_i}{\sum C_i}\right) \times 100 \]

where \(C_i\) and \(\sum C_i\) denote carbon atoms in a compound i and in all the compounds of the reaction product, respectively.

Fig. 2 shows that 100 % conversion was attained at 673 K over ZSM-5 for several hours, then, the conversion was decreased gradually. Fig. 3 shows the selectivity of product types. The main product type was mono-aromatic hydrocarbons with 60 to 65 % selectivity in the earlier stage. Di-aromatic hydrocarbons and other oil products which contain \(C_{10}\) to \(C_{12}\) aromatics were also obtained.
Fig. 4 shows the product selectivity in detail. As mono-aromatics, toluene and xylene were the main products, and the selectivity for benzene and trimethyl-benzene was relatively small. As olefin and paraffin, C_3 and C_4 hydrocarbons were main products as depicted in Fig. 5. Fig. 6 shows a high olefin/paraffin ratio for C_2 and C_3 hydrocarbons. Very high ethylene/ethane ratio was maintained during 10 hours of the experiment. For C_3 hydrocarbons, the selectivity for propane was high compared to that for propylene in the first stage, but the propylene selectivity was increased with time on stream, whereas the propane selectivity was decreased. At first, paraffin formation was favored due to the hydrogen transfer activity of ZSM-5, but olefin/paraffin ratio was increased in the course of reaction.

These results are very similar to those in the conversion of acetone by Tsutsui et al. [8, 11]. Fig. 7 shows a possible mechanism of acetone conversion to aromatic and olefin hydrocarbons. Acetone molecules are successively reacted and condensed by aldol reaction
and dehydration to be converted toward 1,3,5-trimethyl-benzene by ZSM-5 catalyst. Since 1,3,5-tri-methyl-benzene cannot be formed in ZSM-5 pore by the size restriction effect, methyl cation was exchanged by proton which results in the formation of smaller size aromatics such as toluene or xylene and olefin hydrocarbons. This effect of selective formation of smaller size aromatics is thought due to the shape selectivity of ZSM-5. This shape selectivity can also be seen in the composition of trimethylbenzene. Among three isomers, selectivity of 1,2,4-trimethylbenzene is much larger than that of 1,3,5-trimethylbenzene. It is thought that the conversion of EMK proceeds by similar mechanism because the product selectivity pattern in EMK conversion is similar to that in acetone conversion.

### 3.2. Conversion Of Other Ketone And Aldehydes

Figure 8 shows the conversion of various ketones and aldehydes, which can be obtained from biomass by hydrothermal or thermal treatment or fermentation, with ZSM-5.

It is shown in the figure that aromatic compounds and olefin or paraffin hydrocarbons were obtained at very high selectivity from any intermediates used. Major aromatic products were xylene and toluene in common. Total selectivity for aromatics was between 70 and 80%. The aromatic products contained small amount of heavy aromatics such as C10-aromatics or naphthalenes. The selectivity for olefin and paraffin hydrocarbons was 20 to 25%. C3 and C4 hydrocarbons, i.e., propylene, propane, butene and butane were the main products. More olefins were obtained when aldehydes were used. CO and CO2 formation was very small which means very high carbon efficiency in these conversion reactions.

### 3.3. Conversion Of Levulinic Acid

Levulinic acid can be obtained from various biomass such as bagasse of sugar cane or erianthus by hydrothermal treatment with acidic catalyst such as HCl. The result of the conversion of levulinic acid is shown in Fig.9. It is found that product distribution is similar to that in the conversion of ketones or aldehydes except that about 20 C% of CO+CO2, most of which is CO, and more than 10 C% of coke are formed. In the case of carboxylic acid, it can be thought that decarbonylation is necessary to convert it to ketone compounds. It is reasonable that 20 C% CO is formed from levulinic acid, i.e., one carbon atom is converted to CO from five carbon atoms of levulinic acid. The decarbonylated intermediate, hydroxyethylmethylketone, might be unstable and tends to form coke through methylvinylketone formed by dehydration. Hydrogen transfer reactivity of ZSM-5 would convert hydroxyethylmethylketone to ethylmethylketone and finally to aromatic products.
3.4. Conversion Of Oxygen-Containing Intermediates To Aromatic And Olefin/Paraffin Hydrocarbons As Novel Technology For Biorefinery

It is thought that the conversion results described in this work can provide a novel technology for biorefinery in the future if suitable pretreatment such as hydrothermal or thermal conversion [9] or fermentation is combined.

This conversion technology provides wider possibility for the utilization of biomass to supply basic chemicals such as aromatics and olefins or high value fuel components. It means that chemical industry can survive without using petroleum. This technology is a direct, simple conversion method from biomass to basic chemicals, compared to other indirect, complex methods such as the combination of gasification and catalytic processing including methanol synthesis and MTO, etc. or the combination of ethanol fermentation and catalytic processing including dehydration to ethylene and metathesis to propylene, etc.

Carbon efficiency in this biomass conversion may be high compared to other methods such as full fermentation method or gasification-combined method which produce much CO₂.

Another merit of this conversion technology is that the products can be easily separated from water. The biomass-derived intermediates are usually obtained in the mixture with water when either hydrothermal conversion or bio-conversion is utilized at first stage. Therefore, the biomass conversion usually needs a large separation cost to recover the products. The new conversion technology described here does not require much cost for the separation because the reaction can be performed in the existence of water [8, 10] and the products are liquid insoluble to water and gas.

4. Conclusions

1) By catalytic conversion with ZSM-5 zeolite, it was found that oxygen-containing intermediates which can be derived from biomass such as ethylmethylketone, acetone, acetaldehyde, propionaldehyde and levulinic acid were converted to basic chemicals, especially toluene, xylene, propylene, butane, at high yields.

2) This new conversion technology has advantageous features that major products are the most useful base-chemicals in chemical industry, carbon efficiency is high, and products can be separated at a low cost.

3) By combining this reaction with hydrothermal, thermal or fermentation pre-treatment, a novel conversion method from biomass to basic chemicals which are necessary in the conventional petrochemistry can be established.

References


