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Instructions for use

Note

Catalytic Effect of Slags on the Formation of Bio-diesel Fuel

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1. Introduction

Recently, bio-ethanol and the fatty acid methyl ester (FAME, as the bio-diesel fuel (BDF) is called) are widely regarded as clean fuels for motor vehicles. In such circumstances, the BDF, which is formed by the transesterification of vegetable oil, is focused on the alternative fuel for a diesel engine. BDF has a low environmental load, because it has low CO_2 emission after combustion and low SOx and carbon particle formation in comparison with petroleum based diesel oil. Furthermore, it is not counted in the CO_2 emission, since it originated from plants.

At present, the process of BDF production is mainly adopted from the homogeneous reaction system using a liquid alkali hydroxide such as NaOH or KOH.[1] However, it has a few problems such as the production of strong alkali waste water and the generation of soap during water washing processes.
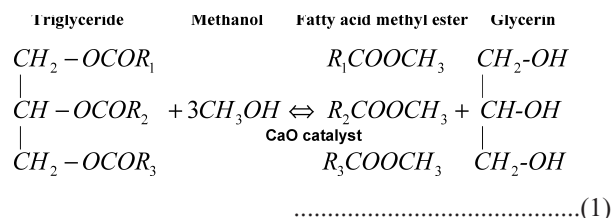
As a result of these problems, a new process of BDF production using solid alkali catalysts, such as CaO, which does not generate the alkali waste water, is desired.[2–4] However, the improvement of surface basicity of CaO is an important problem to overcome due to the fairly low reactivity of the CaO surface in comparison with the liquid catalyst of alkali hydroxide. In another series of the present experiment, modification of the CaO catalyst was performed and the optimum conditions of the treatment of CaO containing materials and the transesterification of fatty acid were obtained.

On the other hand, a large amount of slags in the iron and steel industry in Japan (about 38 million tons per year; 2004 by Nippon Slag Association) are producing as a by-product of iron and steel.[6] The slags are classified into the blast furnace (BF) slag, the converter (LD) slag, and the electric arc furnace (EAF) slag. The BF slag is about 25 million tons, the LD slag is about 9.5 million tons, and the EAF slag is about 3.5 million tons.

Currently, the most of slags are recycled and reused by taking the advantages of the feature of the respective slags (e.g. the BF slag is used for cement and roadbed material, LD slag is also used for the roadbed material and marine

resources, etc.). The quality and quantity of recycle of slags changed greatly within recent ten years and it will be expected as an important resource in the future. However, because of the large amount of slags, the supply always exceeds the demand. It is expected to develop the new way to use the slags.

In this study, the possibility of catalysts of several kinds of slags in the iron and steelmaking process was examined on the basis of the optimum experimental conditions obtained in another experiment using a reagent CaO.

$$
\begin{array}{cccc}
\textit{Triglyceride} & \textit{Methanol} & \textit{Fatty acid methyl ester} & \textit{Glycerin} \\
CH_2-OCOR_1 & & R_1COOCH_3 & CH_2\text{-}OH \\
| & & & | \\
CH-OCOR_2 & +3CH_3OH \Leftrightarrow & R_2COOCH_3 + & CH\text{-}OH \\
| & \text{CaO catalyst} & & | \\
CH_2-OCOR_3 & & R_3COOCH_3 & CH_2\text{-}OH
\end{array}
$$

....(1)

2. Experimental

Figure 1 shows the experimental apparatus for transesterification of fatty acids. A beaker of 300 mL was set on a heating mantle that has a temperature controller. Stirring of the sample mixture (methyl alcohol (99.8%), triglyceride (glycerin ester of fatty acids, so called neutral lipid, which includes most of vegetable oil and animal fats) and catalyst) was performed by an impeller whose rotation speed could be changed up to 2000 rpm. The space between the beaker and the shaft of the impeller was sealed by a rubber cap to prevent the vaporization of methyl alcohol.

The optimum conditions of BDF formation using reagent CaO were obtained and the same conditions were applied for the experiment using slag catalysts that were summarized in the **Table 1**.[5]

In the case of reagent CaO, the amount of catalyst ranged from 2.3 to 5 g and the conditions of transesterification for 100 cm^3 of triglyceride were 20 g methanol, 3 h of reaction

Table 1. Conditions for transesterification of fatty acids and amount of catalyst.

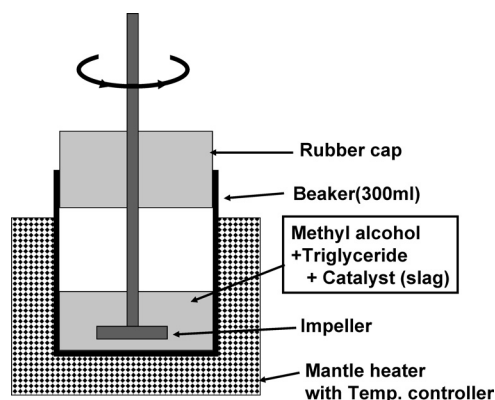| Kind of catalyst	Amount of catalyst	Conditions of transesterification			
		Triglyceride (Vegetable oil)	Methanol	Reaction time	Temp.
CaO	2.3 - 5g	100cm³	20g	3 hours	60ºC
Slags	50g	100cm³	40g	6 hours	60ºC

Fig. 1. Experimental apparatus for transesterification.

Table 2. Chemical composition of slags and basicity.

	CaO	SiO₂	Al₂O₃	MgO	Fe₂O₃	MnO	P₂O₅	S	C/S (CaO/SiO₂)
BF slag	42.99	33.52	13.77	6.28	<0.37	0.27	0.02	0.552	1.28
LD slag	42.85	14.19	2.51	6.97	11.93	3.18	2.38	0.068	3.02

time and 60°C of reaction temperature. On the other hand, the conditions for slag catalyst were 50 g of slag, 40 g of methanol and 6 h of reaction time under same reaction temperature (60°C). The rotation speed of the impeller for stirring was 900 rpm for all runs. The content of methyl esters was analyzed by gas chromatography.

Mainly two kinds of slag were used in the present experiment. One is blast furnace (BF) slag and the other is dephosphorization slag in LD converter (LD slag). The chemical compositions are shown in **Table 2**. The content of CaO in both slags are about 43 mass%. However, as the SiO₂ content of BF slag is higher than that of LD slag, the basicity (C/S ($=$CaO/SiO₂)) of BF slag is 1.28 and C/S of LD slag is 3.02. Although the MgO content is almost the same in the two slags, Al₂O₃, MnO and P₂O₅ are quite different. The mineralogy in the BF slag is relatively simple and two kinds of crystal phases (Gehlenite and Merwinite) precipitate during cooling.[6] The mineralogy of LD slag is complicated and the details will be published in a subsequent paper.

3. Result and Discussion

3.1. Effect of BF Slag

Figure 2 shows the TTT diagram of BF slag obtained by the authors.[6] It was found that the crystal phases precipitated during cooling were Merwinite (3CaO·MgO·2SiO₂) and Gehlenite (2CaO·Al₂O₃·SiO₂). The region of Gehlenite is covered by the one of Merwinite. The nose position of Merwinite in TTT diagram locates at 1 080°C, 4 s. Using this diagram, crystal phase(s) or amorphous phase can be controlled by the cooling rate. In the practical process, most of BF slag is cooled by the water granulated method which results in an amorphous phase. It can be understood from Fig. 2 that a high cooling rate of more than 87°C/s must be attained in the water granulated process (under the assumption of a melt temperature about 1 500°C).

In this experiment, to compare the effect of crystal phase on the formation of methyl esters, the cooling rate was controlled for generating the two crystal phases (Gehlenite and Merwinite). The average cooling rate was about 3.5°C/s (cooling path (2) in Fig. 2), which was attained by the water cooled stainless plate (dry quenched slag).

The two kinds of BF slag were examined by XRD and the results were shown in **Fig. 3**. It was confirmed that the water granulated slag has an amorphous phase and the dry quenched slag has crystal phases consisting of Merwinite and Gehlenite.

Using these two BF slags, the transesterification experiment was performed under the conditions shown in Table 1. The yields of methyl esters are shown in **Fig. 4**. It was found that the water granulated slag had no effect on catalysis of the formation of methyl esters. However, dry quenched slag showed a catalytic effect on the transesterifi-
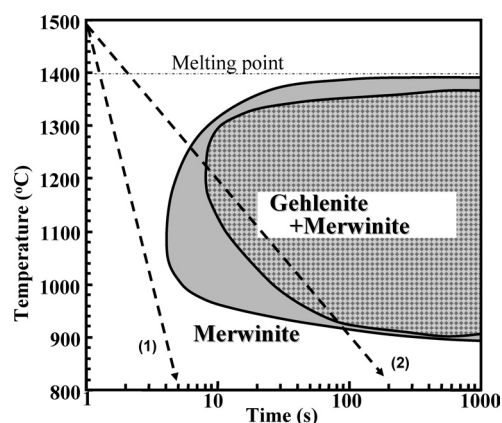
Fig. 2. TTT diagram of BF slag obtained by Kashiwaya *et al.*[6]
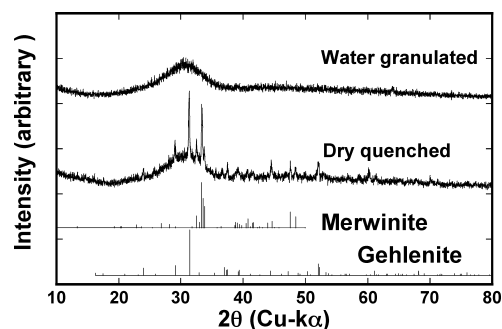
Fig. 3. XRD patterns of BF slag according to different cooling rates (merwinite: 3CaO·MgO·2SiO₂, gehlenite: 2CaO·Al₂O₃·SiO₂).
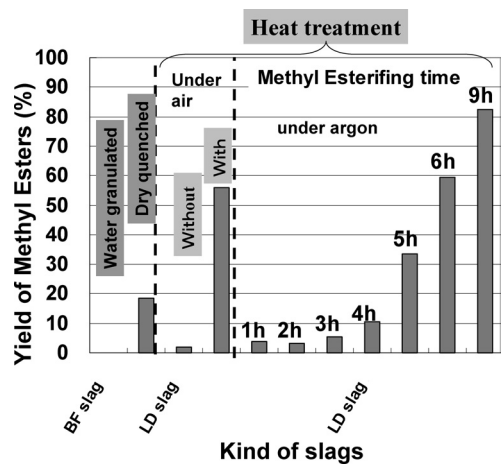
Fig. 4. Yield of methyl esters obtained by different slag catalysts.

cation, although the yield of methyl esters was 18%. This result means the CaO structure on the surface of slag will be important for acting as a catalyst. Generally, it was recognized that the existence of the methoxide, whose reaction is expressed by Eq. (2), could promote the reaction.[1,3]

$$CaO + 2CH_3OH = (CH_3O)_2Ca + H_2O \quad ....(2)$$

Furthermore, the longer experimental time will increase the yield of methyl esters, which would relate to Eq. (2). This result was generally recognized by several kinds of LD slags. The low yield of methyl esters except 0% can increase with longer experimental time, more or less.

3.2. Effect of LD Slag

The LD slag was also used as a catalyst for the transesterification experiment without any heat treatment. Although the yield of methyl esters was only 2%, it increased to 56% due to the heat treatment at 1 000°C, 24 h under air. It is considered that some content of free-CaO in LD slag has already changed to $Ca(OH)_2$ and $CaCO_3$, which do not have a catalytic effect on the transesterification. The heat treatment of LD slag will increase the content of free-CaO by the decomposition reactions of $Ca(OH)_2$ and $CaCO_3$.

The heat treatment at 1 000°C for 24 h under an argon atmosphere was also carried out on the LD slag. The sampling of methyl esters was carried out in 1 h intervals and the analysis of methyl esterification was carried out by gas chromatography. The results were also shown in Fig. 4.

For the first 3 h, the yield of methyl esters was less than 5% and did not increase in this region. However, the yield increased remarkably from 4 to 6 h and the value was about 60% at 6 h. Since the heat treatment under air resulted in 56% methyl esters content for 6 h stirring, the difference in atmosphere for heat treatment was not so important. It is considered that the $CaCO_3$ or $Ca(OH)_2$, which does not have a catalytic effect, will form in the course of cooling and during storage at room temperature. It could be said that the most important factor is the atmosphere for storage of the LD slag. It is important to keep the sample under an inert atmosphere without H_2O and CO_2 for the slag catalyst active.

When the reaction time was increased from 6 to 9 h, the rate of methyl esters formation decreased. This was caused by the vaporization of methanol during stirring by the impeller. Although the space between the shaft of impeller and the beaker was sealed with a rubber cap, a small gap still remained. It was considered that some amount of methyl alcohol will vaporize during stirring and the yield of methyl esters might decrease in the longer time of experiment from 6 to 9 h.

Further experiments are carried out for measuring the activation energy. The results and mechanism of the transesterification with slag will be published in the future.

4. Conclusions

The formation of methyl esters from vegetable oil using two kinds of slag was examined. The optimum conditions for the transesterification using slags were clarified. The effects of slag on the transesterification were measured. The results obtained are as follows.

(1) The water granulated slag does not have a catalytic effect. However, the dry quenched slag whose cooling curve was controlled to generate the crystal phases (Merwinite and Gehlenite) resulted in 18% methyl esters content.

(2) LD slag resulted in only 2% methyl esters content, while the heat treated LD slag at 1 000°C for 24 h under air resulted in 56%. It is considered that some content of free-CaO in LD slag has already changed to $Ca(OH)_2$ and $CaCO_3$, which do not have a catalytic effect on the transesterification. The heat treatment of LD slag will increase the content of CaO by the decomposition reactions of $Ca(OH)_2$ and $CaCO_3$.

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