

Non-catalytic alcoholysis process for production of biodiesel fuel by using bubble column reactor

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Abstract. Biodiesel fuel is a replacement for diesel as a fuel produced from biomass resources. It is usually defined as a fatty acid methyl ester (FAME) derived from vegetable oil or animal fat. In European countries, such as Germany and France, biodiesel fuel is commercially produced mainly from rapeseed oil, whereas in the United States and Argentina, soybean oil is more frequently used. In many other countries such as Japan and countries in Southeast Asia, lipids that cannot be used as a food source could be more suitable materials for the production of biodiesel fuel because its production from edible oils could result in an increase in the price of edible oils, thereby increasing the cost of some foodstuffs. Therefore, used edible oil, lipids contained in waste effluent from the oil milling process, by-products from oil refining process and crude oils from industrial crops such as jatropha could be more promising materials in these countries. The materials available in Japan and Southeast Asia for the production of biodiesel fuel have common characteristics; they contain considerable amount of impurities and are high in free fatty acids (FFA). Superheated methanol vapor (SMV) reactor might be a promising method for biodiesel fuel production utilizing oil feedstock containing FFA such as waste vegetable oil and crude vegetable oil. In the conventional method using alkaline catalyst, FFA contained in waste vegetable oil is known to react with alkaline catalyst such as NaOH and KOH generating saponification products and to inactivate it. Therefore, the FFA needs to be removed from the feedstock prior to the reaction. Removal of the alkaline catalyst after the reaction is also required. In the case of the SMV reactor, the processes for removing FFA prior to the reaction and catalyst after the reaction can be omitted because it requires no catalyst. Nevertheless, detailed study on the productivity of biodiesel fuel produced from waste vegetable oils and other non-edible lipids by use of the SMV reactor has not been examined yet. Therefore, this study aims to investigate the productivity of biodiesel produced from waste vegetable oils using the SMV reactor. Biodiesel fuel is a replacement for diesel as a fuel produced from biomass resources. It is generally produced as a FAME derived from vegetable oil by using alkaline catalyzed alcoholysis process. This alkaline method requires deacidification process prior to the reaction process and the alkaline catalyst removal process after the reaction. Those process increases the total cost of biodiesel fuel production. In order to solve the problems in the conventional alkaline catalyzed alcoholysis process, the authors proposed a non-catalytic alcoholysis process called the Superheated Methanol Vapor (SMV) method with bubble column reactor. So, this study aims to investigate the productivity of biodiesel produced from vegetable oils and other lipids using the SMV method with bubble column reactor.



1. Introduction

Biodiesel fuel is a replacement for diesel (fossil fuel) as a fuel produced from biomass resources. Used edible oil, lipids contained in waste effluent from the oil milling process, by-products from oil refining process and crude oils from industrial crops such as *Jatropha* could be more promising materials for production of biodiesel fuel in Japan and Southeast Asia. Those materials contain considerable amount of impurities and are high in free fatty acids (FFA).

Non-catalytic Superheated methanol vapor (SMV) method using bubble column reactor might be a promising method for biodiesel fuel production utilizing oil feedstock containing FFA such as used vegetable oil and crude vegetable oil [1, 2]. In the conventional method using alkaline catalyst, FFA contained in used vegetable oil is known to react with alkaline catalyst such as NaOH and KOH generating saponification products and to inactivate it. Therefore, the FFA needs to be removed from the feedstock prior to the reaction. Removal of the alkaline catalyst after the reaction is also required. In the case of the SMV reactor, the processes for removing FFA prior to the reaction and catalyst after the reaction can be omitted because it requires no catalyst [3, 4]. Nevertheless, detailed study on the productivity of biodiesel fuel produced from used vegetable oils by using SMV method has not been examined yet. Therefore, this study aims to investigate the productivity of biodiesel produced from used vegetable oils using SMV method with bubble column reactor.

2. Promising materials for production of biodiesel fuel

Biodiesel fuel is a replacement for diesel as a fuel produced from biomass resources. It is usually defined as a fatty acid methyl ester (FAME) derived from vegetable oil or animal fat.

In European countries, such as Germany and France, biodiesel fuel is commercially produced mainly from rapeseed oil, whereas in the United States and Argentina, soybean oil is more frequently used.

In many other countries such as Japan and countries in Southeast Asia, lipids that cannot be used as a food source could be more suitable materials for the production of biodiesel fuel because its production from edible oils could result in an increase in the price of edible oils, thereby increasing the cost of some foodstuffs. Therefore, used edible oil, lipids contained in waste effluent from the oil milling process, by-products from oil refining process and crude oils from industrial crops such as *jatropha* could be more promising materials for use in these countries.

In Japan, it is not feasible to use virgin vegetable oil as a raw material for producing biodiesel fuel because Japan has to import a large quantity of the edible oil from foreign countries. However, it could be possible to utilize used edible oil. In Japan, about 9000 kL/y of FAME is produced from used edible oil and utilized as biodiesel fuel.

Waste effluent from oil milling processes and by-products from oil refining processes contain substantial amounts of lipids. For example, FFA are obtained from the refining process as by-products. The FFA account for 5-10 % of crude oil. These materials are present already and need not be collected. Therefore, if these materials are converted into FAME at a low cost, they could provide a useful source of biodiesel fuel.

Jatropha (Jatropha curcas L.) is an oil crop, which can grow in marginal land such as the eastern part of Indonesia where the amount of rainfall is less than 400 mm/y (Figure 1). The oil content of *jatropha* seeds is 30-40 %. Oil productivity of the *jatropha* plant is considered higher than that of soybean or rapeseed. The first harvest can be obtained within eight months of planting. Then, about 20 kg of seed can be harvested twice a year from one plant. Plant life is about 50 years. However, *jatropha* oil contains toxins and is unsuitable for human consumption. Therefore, utilization of *jatropha* oil in the production of biodiesel does not affect the supply and price of edible oil. If crude *jatropha* oil can be converted into FAME at a low cost, it will be a promising material for biodiesel fuel. Agriculture could therefore be expanded into marginal land by introducing *jatropha* plants, which will benefit the residing communities.

As mentioned above, the materials available in Japan and Southeast Asia for the production of biodiesel fuel have common characteristics; they contain considerable amount of impurities and are high in FFA.

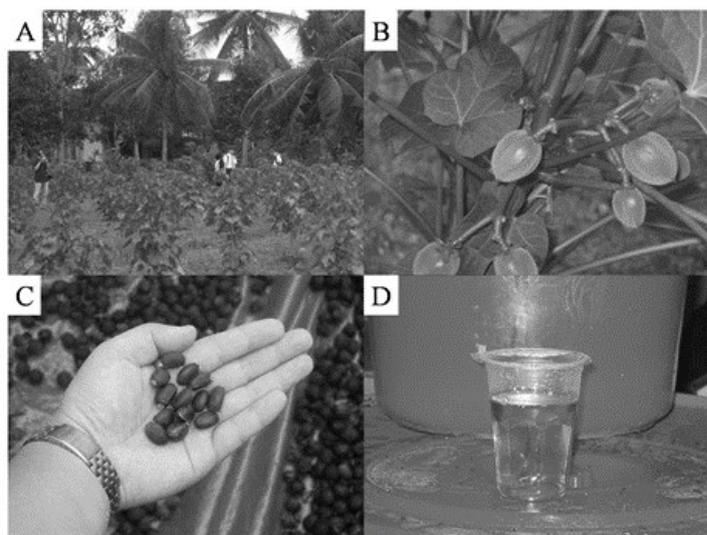


Figure 1. Jatropha plants 6 months after planting (A), fruits (B), seeds (C), and crude oil obtained by screw press (D)..

3. Problems with the conventional alkaline catalyzed alcoholysis reaction process for the production of biodiesel fuel

In the alcoholysis reaction for the production of biodiesel fuel from vegetable oil, triglyceride, which is the main component of vegetable oil, is reacted with methanol to form FAME and glycerol. FAME is used as a biodiesel fuel. In the conventional process, alkaline catalysts such as NaOH and KOH are used to promote the reaction. In the FAME production process using the alkaline catalyst method, the catalyst has to be removed from the products after the reaction. Otherwise, glycerol which is a by-product of the process cannot be utilized directly in other industries. However, the process of removing the alkaline catalyst increases the total cost of biodiesel fuel production.

In the case of the alkaline catalyzed alcoholysis reaction process, FFA contained in raw materials have to be removed prior to the reaction in order to maintain the activity of the catalyst. However, the removal of FFA reduces the yield of the process.

4. Principle and advantages of a novel non-catalytic alcoholysis reaction process called superheated methanol vapor method using bubble column reactor

In order to solve the problems in the conventional alkaline catalyzed alcoholysis reaction process for the production of biodiesel fuel, the authors proposed a non-catalytic alcoholysis reaction process called the superheated methanol vapor method using bubble column reactor.

Figure 2 shows the schematic flow diagram of a reactor for the superheated methanol vapor method using bubble column reactor [1, 2]. Superheated methanol vapor is continuously bubbled into the oil in the reactor vessel and reacted with triglycerides to form FAME and glycerol. The FAME and glycerol formed flows out of the reactor together with unreacted methanol vapor and is collected using a condenser. Condensed FAME is separated from glycerol by sedimentation and used as biodiesel fuel. Unreacted methanol vapor is sent back to the reactor vessel and reused. No catalyst is used in this process.

In a system with the superheated methanol vapor method using bubble column reactor, the purification process to remove the catalyst after the reaction is not required. Therefore, configuration of the total system can be simplified and the by-product, glycerol, can be directly utilized in other industries. In this way, the total cost of biodiesel fuel production will be reduced. Furthermore, triglycerides as well as FFA could be converted into FAME in this method. Therefore, the neutralization process for the removal of FFA is not required prior to the reaction process. This eventually improves

the yield of the total system.

Figure 3 shows the effects of material composition on the outflow rate of FAME in the superheated methanol vapor method. This result shows that not only triglyceride but also FFA can be converted into FAME using this method. The outflow rate is several times higher than that with triglycerides [3, 4]. Furthermore, the result shows that addition of FFA enhances the conversion of triglyceride to FAME. This result implies that this method is suitable for materials available in Japan and Southeast Asia, which are rich in FFA.

In order to confirm the applicability of the superheated methanol vapor method to non-edible crude oils, crude jatropha oil was processed with the method. Crude jatropha oil showed comparable FAME productivity to edible oil such as rapeseed and soybean oils.

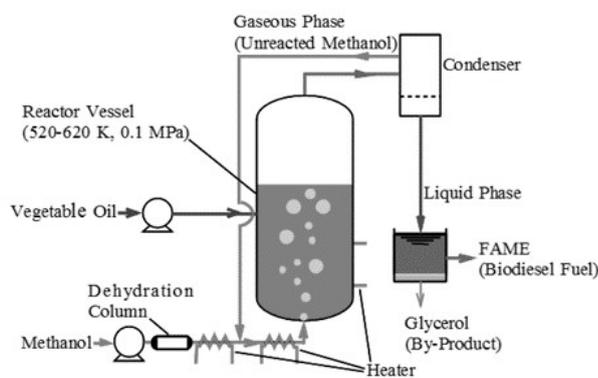


Figure 2. Schematic flow diagram of a reactor based on the superheated methanol vapor bubble method (FAME: fatty acid methyl ester).

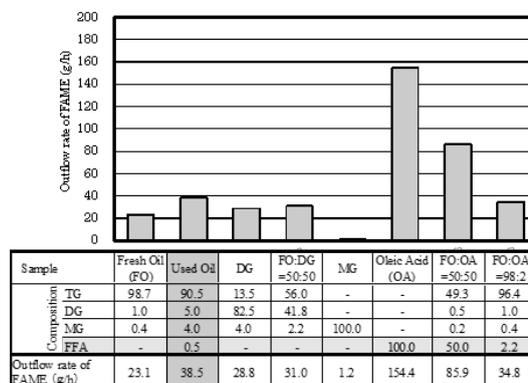


Figure 3. Effects of impurities contained in waste edible oils on outflow rate of fatty acid methyl ester (FAME) from a reactor based on the superheated methanol vapor bubble method (TG: triglyceride. DG: diglyceride. MG: monoglyceride. FFA: free fatty acid.).

5. Economical efficiency of a non-catalytic alcoholysis reaction process using superheated methanol vapor method with bubble column reactor

Eight years ago, the authors' group designed and constructed a demonstration plant based on superheated methanol vapor method (Figure 4). This plant showed 425 L/d productivity of FAME from used frying oil. And energy consumed in each unit of the demonstration plant was measured (electrical energy and thermal energy). Then, based on the energy consumption data obtained with the demonstration plant, production cost required with a practical scale plant (designed productivity: 6000 kL/y) was calculated (Table 1).

The cost required by the practical scale plant with the superheated methanol vapor method was estimated to be 40.6 yen/L (about 40 cent/L) while the cost required by a plant with the alkaline catalyst method was 62.5 yen/L (about 62 cent/L). The estimated cost includes depreciation cost, cost of repairing, labor cost, methanol cost and energy cost (heat and electricity). Most of the energy consumed by the plant was thermal energy and the plant could be automatically controlled. Therefore, required cost will be further decreased by installing the plant next to an incineration facility because thermal energy can be supplied from the facility and the labor cost can also be supported by the facility.



Figure 4. Demonstration plant based on superheated methanol vapor method using bubble column reactor (Designed Productivity: 400 L/d)

Table 1. Estimated cost for production of biodiesel fuel by using superheated methanol vapor method with bubble column reactor

		Demonstration Plant (146 kL/y)	Practical Scale Plant (6 000 kL/y)		Alkaline Catalyst Method (1500 kL/y)
			Basic Case	Combination with an incineration facility	
Depreciation Cost	[yen/kg]	39.2	8.6	8.6	36.1
Cost of Repairing	[yen/kg]	0.9	0.2	0.2	0.8
Labor Cost	[yen/kg]	313.9	7.3	-	7.3
Methanol Cost	[yen/kg]	18.0	10	10.0	25.2
Energy Cost (heat)	[yen/kg]	82.7	13.6	-	1.2
Energy Cost (electricity)	[yen/kg]	28.9	9.7	6.4	1.5
Cost of Catalyst	[yen/kg]	-	-	-	4.1
Total	[yen/kg]	483.6	49.5	28.5	76.1
	[yen/L]	396.5	40.6	23.4	62.5

6. Conclusions

Economical efficiency of a non-catalytic alcoholysis process using bubble column reactor for production of biodiesel fuel was demonstrated in this paper. The authors hope that the results obtained in this research work will reduce the cost involved in producing biodiesel fuel and contribute to the prevention of global warming, reduction in consumption of fossil fuels and the utilization of rural areas in Japan as well as in many other countries.

Acknowledgements

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