초임계 메탄올을 이용한 다양한 식물성 기름으로부터의 바이오디젤 생산

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Biodiesel production from various vegetable oils using supercritical methanol

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Introduction

Biodiesel is defined as the esters of short chain alcohols made from renewable biological source such as vegetable oil and animal fats and it has been given attention as an alternative diesel fuel. There are several methods to produce biodiesel. In conventional biodiesel production, biodiesel is mainly produced in alkali-catalyst condition. However, in this method, there are many disadvantages such as generation of undesired saponified product, problem of water contents, and difficulty of glycerin purification[1]. So, catalyst-free supercritical methanol process are attractive method to overcome such problem. In supercritical process, thermal stability and fuel properties of fatty acid methyl ester(FAME) in extreme condition are important aspect in biodiesel production because synthesis is carried out in high temperature and high pressure[2]. In addition, due to variety of the biodiesel source, it is important to investigate tendency on how the various fatty acid profiles of the different sources can influence biodiesel fuel properties. In this study, thermal stability and properties of biodiesel according to degree of unsaturation of vegetable oil are studied for prevention of thermal degradation in supercritical process

Experimental

The vegetable oils experimented in this study were palm oil, rapeseed oil, soybean oil, safflower oil and flaxseed oil. They have different chemical compositions of fatty acids in their triglycerides as in Table 1[3]. The reagent synthesized with vegetable oils was methanol. Synthesis of biodiesel using supercritical methanol was carried out in batch reactor made by SUS 316. Temperature was controlled by molten salt bath and pressure was controlled by amount of reagents calculated using NIST Chemisty WebBook data[4]. The range of temperature was from 250 ℃ to 400 ℃. and the reaction time was 5, 10, 30, 60 min. The pressure was fixed 35 MPa. The molar ratio of methanol to vegetable oil was fixed 40. To stop the reaction, after the reaction, the batch reactor was quenched by the immersing the reactor in a ice water bath. To remove the unreacted methanol, the crude product containing methanol was evaporated at 70 ℃ in Force Convection Oven during 12 hours. After evaporation, to separate FAMEs from glycerol centrifugation was operated and then obtained product was analyzed by gas chromatography according to the KS M 2413. The instrument was Agilent 6890 and HP-INNOWax (30m×0.32mm×0.2μm) capillary column was used.

Table 1. Fatty acid composition of various oils used in this study.

oils	Fatty acid composition (wt%)				
	16:0	18:0	18:1	18:2	18:3
palm	42.6	4.4	40.5	10.1	0.2
rapeseed	3.5	0.9	64.1	22.3	8.2
soybean	13.9	2.1	23.2	56.2	4.6
safflower	7.3	1.9	13.6	77.2	0
flaxseed	5.1	2.5	18.9	18.1	55.1

Results and discussion

To study the thermal stability of various fatty acid methyl ester in supercritical process, 5 kinds of oils which have different fatty acid composition were experimented at various experimental condition. In these experiments, the influence of reaction temperature and reaction time is shown in Fig 1. When the reaction temperature was lower than 300℃(a,b), the FAMEs contents increased with the increase of reaction time. On the other hands, above 35 0℃(c,d), the FAMEs contents increased according to the reaction time at the short time. After highest point yield of the reaction, the FAMEs contents decreased with the reaction time.

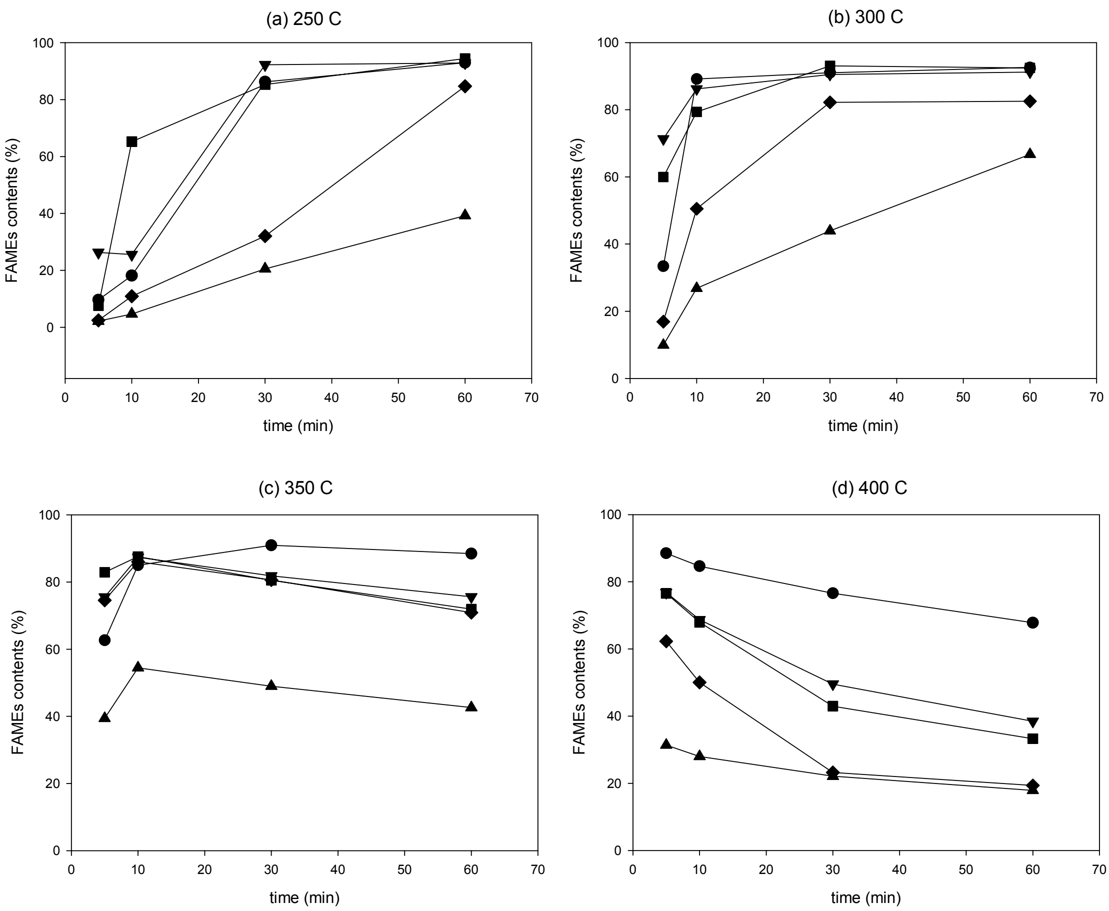

Fig 1. FAMEs contents of different 5 vegetable oils at various reaction temperature and reaction time : ● palm oil; ▼ rapeseed oil; ■ soybean oil; ◆ safflower oil; ▲ flaxseed oil (P: 35MPa, molar ratio: 40:1)

From this results, we found that the decrease of the FAMEs contents after critical point of reaction time at high temperature was due to loss of unsaturated FAMEs[5]. At extreme experimental condition, there were side reactions, such as thermal decomposition reaction, dehydrogenation reaction and peroxidation reaction[5,6]. The variation of main fatty acid methyl ester from different vegetable oils according to the reaction conditions indicated in Fig 2. At mild condition, the FAMEs contents of all biodiesel increased with reaction time. On the other hands, at high temperature, the FAMEs contents of saturated FAME(16:0) from palm oil(a) was almost never changed with reaction temperature and reaction time. In the case of mono-unsaturated FAME(18:1) from rapeseed oil(b), there was decrease of the FAMEs contents with the increase of the reaction time. For poly-unsaturated FAMEs(18:2, 18:3) from soybean oil(c), safflower oil(d) and flaxseed oil(e), decomposition occurred significantly and had influence on loss of the FAMEs contents. These results are matched with the results of the Fig 1. As the amount of unsaturated FAMEs are increased, the thermal stability of biodiesel at extreme condition such as high temperature and long reaction time is poor.

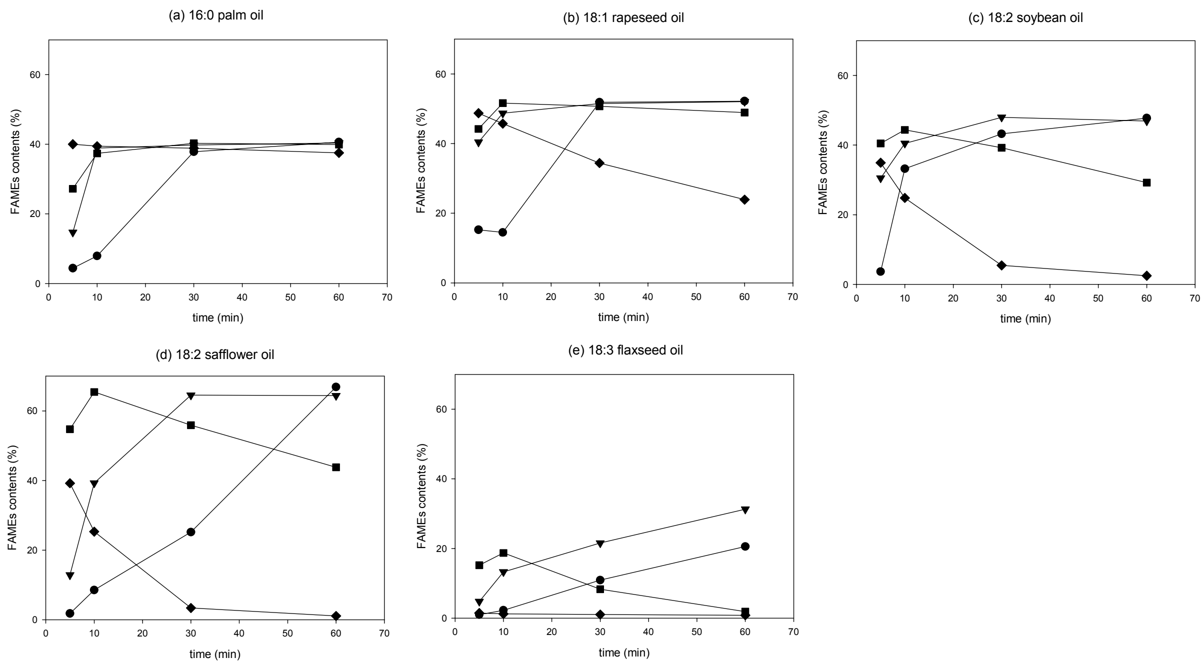

Fig 2. Yield of each FAMEs from different 5 vegetable oils at various reaction temperature and reaction time : ● 250℃; ▼ 300℃; ■ 350℃; ◆ 400℃ (P: 35MPa, molar ratio: 40:1)

Conclusion

To reduce the loss of biodiesel in supercritical process, the study of the thermal stability and the fuel properties of various vegetable oil are conducted. As a results, the amount of unsaturated fatty acid in the vegetable oil was related to the loss of biodiesel at extreme condition due to its thermal stability. In other words, unsaturated fatty acid methyl esters were dramatically decomposed above 350℃, whereas saturated fatty acid methyl ester did not change at same condition of unsaturated FAMEs. Therefore, in biodiesel production using supercritical methanol, selection of vegetable oil and reaction condition is very important factor in order to decrease the loss of yield.

Reference

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