바이오디젤의 열적특성에 관한 연구

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A Study on Thermal Characteristics of Biodiesel

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Abstract : A study is conducted on thermal characteristics of biodiesel which is already being produced in many countries because of its stable supply of energy in non oil-producing countries and economical benefits against increasing oil price, and environment conservation. So biodiesel has been used as important energy source in the fuel fields and a mount of production has increased year by year. Therefore, it is very important to find out the thermal characteristics of biodiesel for ignition temperature, maximum pressure and thermal behavior. The purpose of this study is to compare on thermal characteristics of biodiesel, petroleum diesel and those mixtures. Also, the main study was performed by flash point testers and modified closed type of pressure vessel test (MCPVT). Based on the data of flash point and MCPVT, the ignition temperature and the maximum pressure of biodiesel was 182℃ and 40.1bar, and petroleum diesel was 54℃ and 29.8bar.

초 록 : 세계적으로 대기환경문제와 원유가격의 상승 그리고 비산유국의 안정적인 에너지공급의 대체에너지로서 부각된 바이오디젤은 현재까지 많은 연구가 진행되어 왔으나, 온도변화에 대한 열적거동에 관한 연구는 국내에서 수행되지 못했다. 따라서 본 연구에서는 일반디젤과 바이오디젤 그리고 이들 혼합물질의 인화점, 열분해 압력 그리고 열적 거동에 관한 연구를 수행하였으며, 그 결과 인화점과 열분해 압력변화에 있어서 바이오디젤은 일반디젤에 비해 인화점은 182℃로 일반디젤의 54℃ 보다 많이 높으며, 열분해압력도 바이오디젤의 경우 40.1bar, 일반디젤의 경우 29.8bar로 바이오디젤의 열적 안정성이 상당히 높은 것으로 나타났다.
Key Words : biodiesel, petroleum diesel, thermal characteristic, flash point

1. Introduction

It is important to understand thermal characteristic as a method to estimate the danger of chemical material, because the change patterns of material varies with temperature change. Actually, it is not too much to say that each pattern is different according to the kinds of materials.

Particularly, Biodiesel is a renewable diesel fuel (petroleum diesel was called petrodiesel in this paper) substitute that can be made from vegetable oils or animal fats. Though several different kinds of fuels are called biodiesel, usually biodiesel refers to an ester or oxygenation, made from the oil and methanol[1)].

An understanding of soybean biodiesel characteristics requires an understanding of the chemical make up of biodiesel and its parent, vegetable oil. Any vegetable oil contains a glycerol molecule bonded to three fatty acid chains. This structure can be called a trimester or triglyceride. But different oils may contain different types of fatty acid chains. Biodiesel produced from different source oils may contain different proportions and types of fatty acid chains[2)].

However vegetable oils and biodiesel are not hydrocarbons because oxygen atoms exist in the chemical structure while gasoline and petrodiesel are true hy-

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drocarbons as they contain molecules like iso-octane and cetane[3]. Therefore, biodiesel and petrodiesel are different fuels from the nature of those matters.

Biodiesel is one of the next generation energy, in particular, due to its environmental benefits in comparison to petroleum based fuels: biodiesel reduces emissions of carbon dioxide by approximately 50% on a net lifecycle basis[4]. Moreover, it can be stably supplied in non oil-producing countries, to cope with the increasing price of crude oil.

Therefore, it is estimated that the production and consumption of biodiesel must increase more and more than before. So biodiesel and petrodiesel are being used together but the danger of these fuels should be studied. In this study used soybean biodiesel because many American and Asian countries biodiesel is made from soybean oil[5].

The purpose of this study is to compare combustion property of biodiesel with that of petrodiesel. The important parameters of thermal characteristics of using flash point testers and modified closed type of pressure vessel test are flash point, maximum pressure and thermal behavior which may offer useful data to the new fuel fields.

2. Sample

In this study, among various biodiesels available, soybean biodiesel (soybean biodiesel was called biodiesel in this paper) was used in test. Biodiesel is produced in Gyeonggi-do, Korea. Petrodiesel is generally available commercially was used in the test too. Table 1 shows the chemical and physical characteristics of biodiesel and petrodiesel.

The results of density, dynamic viscosity and boiling point of biodiesel are higher than petrodiesel is

Table 1. Chemical and physical characteristics

Item	Unit	Bio Diesel*	Petro Diesel**
Density	kg/m^3	884	810
Dynamic viscosity	mm^2/s	4.15	3.26
Pour point	℃	-2.0	-
Boiling point	℃	320	160
Vapor pressure	mmHg	0.71	0.40
Color	-	Clarity yellow	Clarity green

* Ref. by MSDS of manufacturing company.
** Ref. by MSDS of petroleum oil company.

Table 2. Mixing ratio of biodiesel and petrodiesel (Volume, %)

Name	Biodiesel	Petrodiesel
Bio-100	100	Non
Bio-70	70	30
Bio-50	50	50
Bio-30	30	70
Bio-20	20	80
Bio-10	10	90
Bio-5	5	95
Petrodiesel or Bio-0	Non	100

that molecular weight of biodiesel is usually lager than petrodiesel.

Table 2 shows the mixing ratio of biodiesel and petrodiesel in test samples. The reason of carrying out the experiment by this ratio is that data which obtain whole tendency of mixed ratio are needed in that most of the countries adopt the method of mixing biodiesel and petrodiesel by some different ratio.

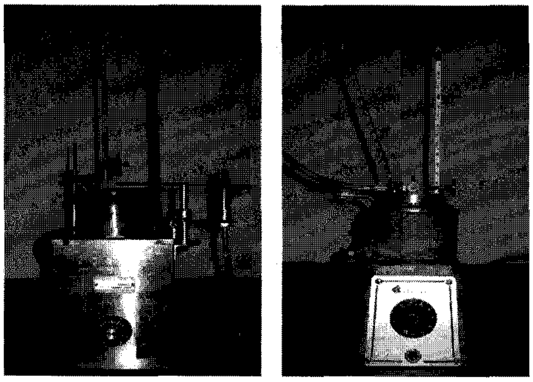
3. Apparatus and Method

3.1. Flash point tester

The measuring flash points are two basic types of flash point measurement: open cup and closed cup. In open cup devices the sample is contained in an open cup which is heated, and at intervals a flame is brought over the surface. The measured flash point will actually vary with the height of the flame above the liquid surface. A closed cup testers, of which the Tag closed cup is one example, are sealed with a lid through which the ignition source can be introduced periodically. The vapor above the liquid is assumed to be in reasonable equilibrium with the liquid. Closed cup testers give lower values for the flash point[6] and are a better approximation to the temperature at which the vapor pressure reaches the lower flammable limit. The flash point is an experimental measurement rather than a fundamental physical parameter.

In this study used two kinds of the flash point testers which are show in Fig. 1.

In Fig. 1, A is the Cleveland open cup tester which conforms to ASTM D92, B is the tag closed cup tester conforms to ASTM D56. Those were consisted a basis of test flame applicator, sample cup, thermometer support, heating plate and electric heater. Spe-



(a) (b)

(a) Cleveland open cup tester
(b) Tag closed cup tester

Fig. 1. Pictures of the flash point testers.

cially, tag closed cup tester has upper lid on sample cup. Also, Cleveland open cup tester excepts an open cup flash below 79℃ and the tag closed cup tester can determinations of liquids with a viscosity of below 5.5cSt at 40℃ or below 9.5cSt at 25℃, and a flash point below 93℃.

In case of Cleveland open cup tester, the flashing point was measured by putting a sample 80mL into a sample cup and increasing temperature at the rate of 5℃/min. In measuring a sample which has the flashing point less than 60℃, the flashing point was measured by increasing temperature at a rate of 1℃/min and measured every 0.5℃. When the flashing point of a sample was more than 60℃, the flashing point was measured every 1℃, increasing temperature at a rate of 3℃/min.

3.2. MCPVT

A modified closed type of pressure vessel test (MCPVT) is the newest type analysis equipment, which are screening methods for testing the effects of liquid and solid chemical compounds when heated up under confinement. Special emphasis is laid on the observation of the resulting pressure build-up. Also MCPVT can measure maximum pressure, maximum rate of pressure rise, onset temperature of the decomposition reaction and maximum temperature during overall reaction with small amount of sample. The MCPVT equipment shows in Fig. 2 and consist an electric furnace of PID type, sample vessel, amplifier

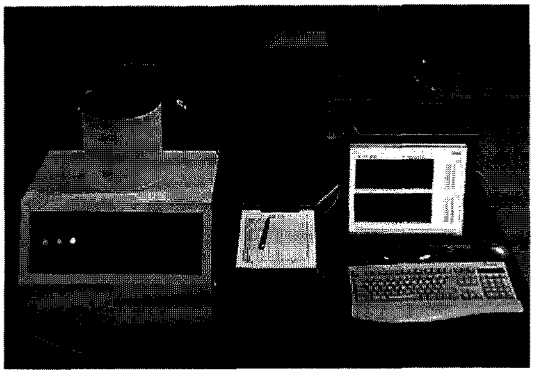


Fig. 2. Picture of MCPVT tester.

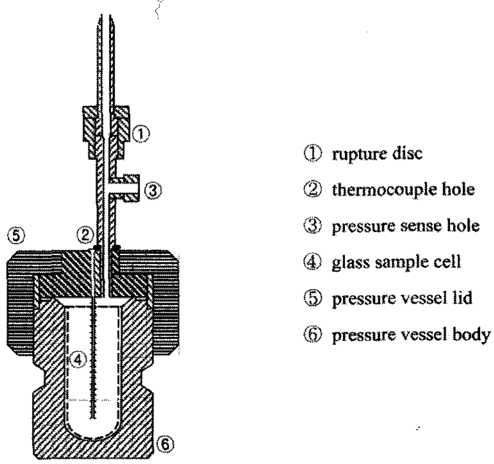


Fig. 3. Cross section of MCPVT sample vessel.

of pressure signal and computer for setup control and data saving.

Fig. 3 shows a cross section of MCPVT sample vessel and the composition of glass sample cell, thermocouple, pressure sense, pressure vessel lid part and body part.

The experiment order is that 1±0.1g sample is put in a sample cell, which is a 6mL-cylinder made of glass and sample bath made of stainless is put in it. Next, the vessel lid should be locked completely. And then, tuning check valve toward rupture disk, the air in and out of vessel should be blocked. After inputting setting temperature on temperature controller, the heating rate was 5℃/min.

4. Results and Discussion

4.1. Flash point tester

The flash point definition is that of a flammable liquid is the lowest temperature at which it can form an ignitable mixture in air. At this temperature the vapor may cease to burn when the source of ignition is removed. So every flammable liquid has a vapor pressure, which is a function of that liquid's temperature. As the temperature increases, the vapor pressure increases. As the vapor pressure increases, the concentration of evaporated flammable liquid in the air increases. Hence, temperature determines the concentration of evaporated flammable liquid in the air under equilibrium conditions. Different flammable liquids require different concentrations of the fuel in air to sustain combustion. The flash point is that minimum temperature at which there is a sufficient concentration of evaporated fuel in the air for combustion to propagate after an ignition source has been introduced.

Fig. 4 shows the flash point results of biodiesel mixtures by the Cleveland open cup, the flash point changes according to the maxing ratio of biodiesel.

The result of Fig. 4 shows that petrodiesel was the flashing point 58℃ and pure biodiesel was the flashing point 182℃. And in the section of biodiesel mixing ratio 0~10%, proportion of a flashing point increased regularly, while that of a flashing point more slowly increased in the section 10%-30%. And it began to increase regularly in 30~70% again. In the section over 70%, a flashing point increased sharply. It is estimated that biodiesel having relatively larger molecular weight has a tendency to have a higher flashing point.

Fig. 5 shows a comparison of the flash point results of the Cleveland open cup and tag closed cup. The reason that both of experiment assemblies were used is that whole flashing point can be measured by Cleveland open cup tester (see in fig. 4) owing to the high flashing point 182℃ of biodiesel. But in case that biodiesel mixing proportion is lower, accurate measuring is difficult because Cleveland open cup tester flashing point is out of measurement range (only over 80℃ is possible). In case of tag closed cup tester, since flashing point can be measured below 93℃, the flashing point of mixture that contains less amount of pertodiesel and biodiesel is difficult to measure. Therefore, both Cleveland open cup and tag closed cup testers were used to obtain the more accurate flashing point.

The result of flashing point tag closed cup tester had a lower flashing point than Cleveland open cup tester. In petrodiese, the result of tag closed cup tester was 54℃, which is 4℃ less than that of Cleveland open cup tester. But, in mixing proportion 30%, the result values of Cleveland open cup tester and tag closed cup tester was the similar. In experiment of the section over 60℃, temperature rising rate of tag closed cup tester changed 1℃/min into 3℃/min in this changed section, which is biodiesel mixing proportion 5%, the difference of tag closed cup tester and Cleveland open cup tester grew to smaller and they came to have nearly the same flashing point at 30%. But From the section 50%, the difference of tag closed cup tester and Cleveland open cup tester grew to be larger.

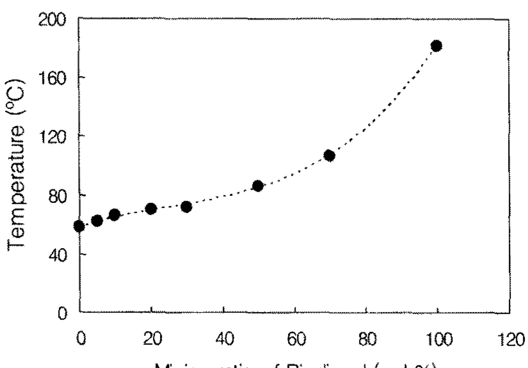


Fig. 4. Flash point results of biodiesel mixtures by Cleveland open cup.

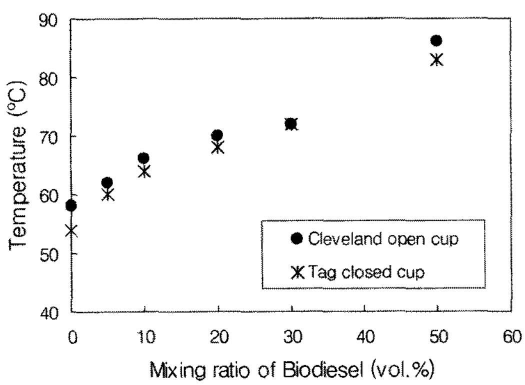


Fig. 5. Comparison of the flash point results of Cleveland open cup and tag closed cup.

4.2. MCPVT

A modified closed type of pressure vessel test (MCPVT) which can analysis of temperature behavior during overall reaction. In Fig. 6 shows the time history of samples temperature.

The result in Fig. 6 shows that two type temperature curves of biodiesel mixtures and petrodiesel. That is to say, regardless of proportion of biodiesel mixture, temperature curves of biodiesel stay the same. In case of petrodiesel has a curve in a lower temperature than that of biodiesel. The reason that temperature variation curve stays the same in biodiesel mixtures heat emission by burning of 1g of an amount occurred through the wall of MCPVT sample vessel which is made of stainless steel. The reason is that inner temperature of the container is higher than heating speed.

Fig. 7 shows time history of samples pressure and pressure grew up slower about 4500second and became maximum pressure about 8000second. Here, maximum pressure of pure biodiesel was 40.1bar.

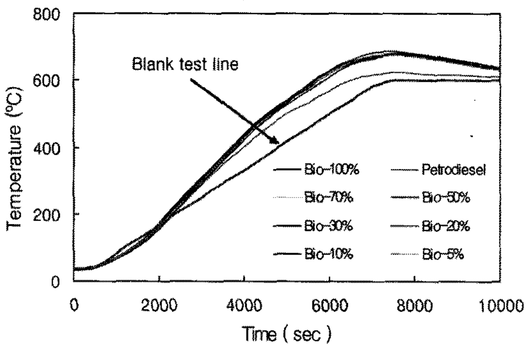


Fig. 6. Time history of samples temperature.

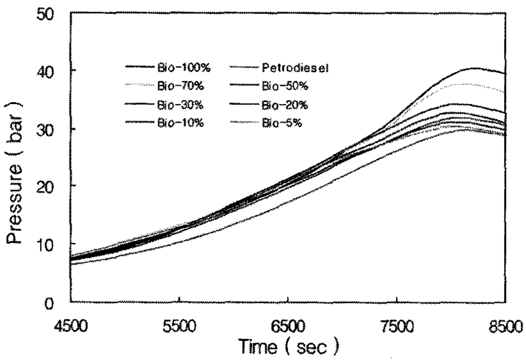


Fig. 7. Time history of samples pressure.

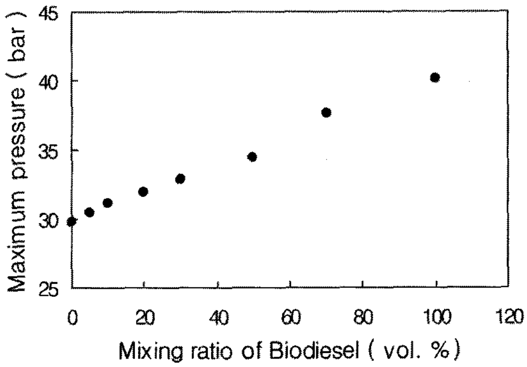


Fig. 8. Maximum pressure of biodiesel mixtures.

According to lowering biodiesel mixing proportion, pressure decreased into 37.6bar, 34.4bar, 32.8bar, 31.9 bar, 31.2bar, 30.5bar. And the state of only petrodiesel was 29.8bar which is the lowest. Maximum pressures acquired by this result are shown in Fig. 8.

The reason that the result of Fig. 8 shows the higher biodiesel proportion is, a higher maximum pressure is that biodiesel whose density and boiling point are higher as well as molecular weight comparing to petrodiesel emits much more heat when burning.

5. Conclusion

In order to understand on thermal characteristics of biodiesel is important because it is an alternative fuel pursued word wide. This study was performed by Cleveland open cup and tag closed cup flash point testers and modified closed type of pressure vessel test (MCPVT) with using soybean biodiesel, petroleum diesel and those mixtures.

The flash point results of soybean biodiesel mixtures by the Cleveland open cup, the flash point changes according to the maxing ratio of soybean biodiesel, petroleum diesel was the flashing point 58℃ and pure soybean biodiesel was the flashing point 182℃. The result of flashing point tag closed cup tester had a lower flashing point than Cleveland open cup tester, in petroleum diesel was 54℃, which is 4℃ less than that of Cleveland open cup tester. In MCPVT, maximum pressure of pure soybean biodiesel was 40.1bar. According to lowering biodiesel mixing proportion shown pressure decreased, and only petroleum diesel was 29.8bar.

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