Biodiesel Production Using Co-solvent

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1. Summary

Biodiesel (fatty acid methyl ester), which is derived from triglycerides by transesterification with alcohol, has attracted considerable attention during the past decades as a renewable, biodegradable, non toxic fuel. Several processes for biodiesel fuel production have been developed, among which the transesterification using alkali catalysis gives high yields of conversion. The main problem of transesterification reaction is that the reactants are not readily miscible. This leads a longer reaction time and so higher fixed capital investments and product costs. Introducing a mixing solvent agent such as THF (tetrahydrofuran), enables the reaction to be one phase. Therefore, complete conversion is achieved up to 99.89 wt% in very short reaction time such as 10 minutes. In this report, the results of the experiments, which are carried out in the Quality Control Laboratory of Fox Petroli SPA Vasto Plant, are published. The experiments are performed to see optimum conditions of this solvent using technique. The results would lead lower capital investments and operating expenses for biodiesel production.

Keywords: Biodiesel fuel, solvent, base – catalyzed methanolysis

2. Extended Abstract

The transesterfication process is a well known process to produce fatty acid methyl esters from vegetable and animal based oil. Reaction conditions for the transesterfication reaction is conventionally 60°C and 1 atm pressure, the medium is mixed generally in a batch type processor. However, since the reaction of fatty acids with methanol is reversible, the reaction comes to equilibrium before a complete conversion of the oil. This is why an extent amount of methanol is added to the reaction mixture, in order to shift the equilibrium the product side. Adding more methanol is not a solution by itself since for complete reaction impractical amounts of methanol may be needed for a high conversion degree [1].

The rate of reaction decreases as approaching the equilibrium. The main problem for the lower rate of transesterification is that the reaction mixture is not homogeneous because the oils and alcohols are not miscible each other because of their chemical structures. Oil disperses in the methanol medium, so the probability and the rate of collision of the glyceride and the methoxide (the mixture of methanol and the alkaline catalyst – KOH or NaOH) molecules becomes lower. This lowers the rate of collisions of molecules and so the rate of reaction causes longer reaction times, higher

operating expenses and labor. For example, the current technology used commercially in one of the biggest biodiesel supplier in Europe includes two step reactions in series which are 1 hour and 30 min respectively. The glycerin is removed after first reaction and fresh methoxide is added more for the second reaction. This means approximately 2 hour reaction time which is long and laborious because of batch process. This technology needs a significant amount of fixed capital investment since the volumes of equipment are huge compared to a continuous process.

To overcome this difficulty of the heterogeneous mixing of the reactants, a single phase reaction has been proposed by Boocock et al [2]. The proposed model includes a cyclic solvent introduced into the reaction mixture which makes both the oil and methanol miscible. This solvent can be a numerous of different solvents with the boiling point up to 100°C. THF (tetrahydrofuran) is preferred because of close boiling point to that of methanol so that after reaction both methanol and THF can be recycled in a single step to use again.

Materials and methods
All the materials used are those being processed in the plant; colza oil, methanol, KOH and 99.7% pure THF. Various reaction conditions, such as reaction time and volume ratios are investigated to find optimum conditions. The fixed reaction conditions are the temperature 23°C, the room temperature (no heating required), atmospheric pressure (1 atm), and there was no mixing needed except the initial gentle mixing. Samples are removed from the reaction mixture and washed with deionized water immediately to stop the reaction and then the samples are injected in the Gas Chromatograph (GC) to determine the mono-, di-, tri- and the free glycerin content of the product. The operating conditions of GC is set as the European Standart by CEN/TC 307 [3].

Results and discussions
Initial experiment is carried out by using the following molar ratio of oil:Methanol:THF ; 1:1:1. First, the KOH is dissolved in the methanol. At the same time, the oil and THF is poured in the beaker and then the catalyst mixture is added to the medium. Samples are taken from the mixture for 3, 5, 10 and 20 minutes. The amounts of samples are small enough for not changing the concentration of the reaction medium. The samples are diluted for the GC injection and analyzed for the conversion to methyl ester. Table 1 shows the results on GC analysis in terms of weight percents.

Table 1. The results of Gas Chromatography for the 1st run

Time (min)	Mono- (wt%)	Di- (wt%)	Tri- (wt%)	Free glycerin (wt%)	Metylester (wt%)
3	2.69	0.54	0.25	0.0008	95.72
5	1.11	0.08	0.01	0.0027	98.01
10	1.24	0.03	0.01	0.001	98.51
20	0.89	0.05	0.01	0.0029	98.79

Since the reaction is quite fast and reaches equilibrium in a small amount of time like in 5 minutes, there is a nearly complete conversion of tri- and di- glycerides. After 20 min, the weight percent of the mono- in the reaction medium is around 0.8% which is acceptable in EN and ASTM standards aspects.

In order to guess the optimum amount of THF that is to be used for one phase homogeneous reaction mixture; different amounts of THF are used. The two volume ratios of oil to THF investigated are 1:0.5 and 1:0.25. The samples are taken from the mixture at 5 and 10 minutes. All the other reaction conditions are the same except THF volume ratio. First, the volume ratio of 1:0.25 is added to the reaction mixture and the GC results are as in Table 2.

Table 2. Chromatograph results Oil:THF volume ratio 1:0.25

Time (min)	Mono- (wt%)	Di- (wt%)	Tri- (wt%)	Free glycerin (wt%)	Metylester (wt%)
5	4.01	6.31	2.23	0.0108	85.25
10	2.21	0.37	0.01	0.019	96.76

As it can be seen on the table, the amount of THF is not enough to make the reaction medium one phase so that the reaction is completed in 10 minutes. After 5 minutes 80% of mass conversion is achieved. This amount of THF (1:0.25) does not make the reactants miscible.

Then the volume ratio 1:0.5 is added to the reaction mixture and the GC results are as in Table 3.

Table 3. Chromatograph results Oil:THF volume ratio 1:0.5

Time (min)	Mono- (wt%)	Di- (wt%)	Tri- (wt%)	Free glycerin (wt%)	Metylester (wt%)
5	2.37	1.1	0.84	0.0121	94.81
10	**0.05**	**0.03**	**0.01**	**0.0029**	**99.89**

Near complete conversion is achieved for this run. As it is seen on the table, there is very small amount of mono- and there is no di- and tri- detected. Therefore, these conditions proposed to be the optimum.

Using such a process in industrial scale has many advantages. First of all, a continuous process is possible. Secondly, the sizes of the equipment expected to be very small when compared to the batch type processing equipment. This means a lower capital fixed cost is needed when constructing a new biodiesel plant. Another obvious advantage of this process is that the operating expenses are lowered. In batch processes, more labor needed and the production needs more time. In an existing biodiesel plant in Italy, 10 m^3 of reactors are used in series to produce max 18,000 kg/h biodiesel and the total reaction time is around 2 h [4].

Conclusions

In this study, experimental results of a novel method of biodiesel production are introduced. This method includes a solvent which makes the reactants oil and methanol enable to be miscible. Therefore, this homogeneous single phase reaction medium leads to a very fast reaction when compared to conventional reaction times. Complete reaction is possible in only 10 minutes.

The experiments are carried out in the quality control laboratory of Fox Petroli SPA, Vasto Plant. Different sets of run is performed to determine the optimum amount of solvent needed for the single phase fast reaction and also to decide the optimum reaction time. It is concluded that industrial scale demonstrations of this technique is possible with lower capital investments and operating costs.

Acknowledgements

References

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