BİODİZEL MESELESİ

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ÖZET

Biodizel günümüzün en popüler alternatif yakıtlarından biridir. Makalede biodizelin üretim prosesi, alternatif yakıt olarak değeri, ne kadar alternatif olduğu mevzuları irdelenmektedir. Makalede biodizel üretiminde kullanılan prosesler sırayla tanımlanıp;

a) Baz katalizi ile transesterleme
b) Asit katalizi ile transesterleme
c) Lipaz enzimi uygulanması
d) Proliz
e) Mikrodalga uygulanması
f) Ultrasonik ses uygulanması

Gibi prosesler mukayese edilmekte, en uygun prosesin tanımlanmasına çalışılmaktadır.

Biodizelin zannedildiği gibi motorine alternatif olamayacağı, dünya tarım arazilerinin ancak küçük bir kısmının biodizel için yağ bitkileri üretmeye ayrılabileceği, bunun dışındaki söylentilerin gerçekleri yansıtmadığı vurgulanmaktadır. Biodizel ekonomisi irdelenmekte, verimi artırma ve maliyeti düşürme yolları araştırılmaktadır.

Yazıda biodizelin üretim ve saglaştıma koşulları, araçlarda kullanılmasının ne gibi sonuçlar doğuracağı gibi mevzular da irdelenmektedir.

-Biodiesel Production by Transesterification- A Review

By Mehmet Mutlu Özdemir

Abstract:

As worlds energy need increases and amount of fossil fuels decrease; needs for new energy supplies occur. Biodiesel is one of environment friendly and renewable energy source alternatives. Biodiesel production is made by pyrolysis, transesterification and lipase catalysis. Transesterification is the most common one. New energy performing techniques are needed in order to get higher yields in less time. Ultrasound and microwaves seem to be best reaction medium alternatives for biodiesel production.

Keywords: Biodiesel; Kinetics; Methanolysis; tranesesterification; ultrasound; microwaves; pyrolysis; fatty acid; methyl esters; anternative energy

Introduction:

Biodiesel is one of the most important alternative fuels in our time. However it is said that the solution to world's energy problem is the hydrogen energy, today we do not have the technology to produce the cheap hydrogen we need. Sometimes it is said that water is the best and cheap source for hydrogen. That is nonsense because the energy needed for the electrolysis of water is more than the actual energy obtained by burning the hydrogen produced. As biodiesel is a renewable source based on agricultural raw material, it is a better alternative with todays technology. As plants do grow by photosynthesis, the CO_2 released to atmosphere by biodiesel combustion would not cause greenhouse effect.

Some label biodiesel as an ethically wrong fuel. They claim that food must not be used for transportation. Here there is an oil insufficiency for biodiesel production. To solve this problem oil farming for industrial use is necessary. Today palm oil and canola seem to be good future sources as biodiesel feedstock. If we consider the annual diesel fuel of the world, biodiesel is today very far from being an alternative for petroleum based diesel fuel in quantity. That makes new researchs for making inventions in oil farming necessary.

Procedure:

Biodiesel is the liquid fuel with about 10 times less viscosity than the oil. As it has viscosity values similar to diesel fuel (1.5-2x) and , higher cetane numbers it is okey for using in diesel engines. Transesterification is a very old and common method for decreasing the viscosity of oil. The most common style of transesterification is transesterifying the dry oil with methanol in presence of alkali catalysis. Here NaOH is the most commonly used catalyst as it is very commonly and economically available while giving high yields of conversion to biodiesel. KOH can be used as an alternative to NaOH in order to obtain K_3PO_4 which can be used as fertilizer after the transesterification is completed. This makes KOH economically charming. $Ba(OH)_2$ is also a good catalyst with yields near to those of NaOH and KOH. As it is a heterogenous catalyst for the transesterification reaction, it makes purification of the glycerol obtained easier. It can also be recovered by filtration and reused.

The best reaction medium is at about 60 C and high speed agitation. Stirring is very important that if there's no emulsion , there'd be no reaction. Reactor must be close covered in order to prevent methanol evaporation. Maybe some organometallic ocmplexes with similar properties to alkali bases can be used as catalysts in transesterification of oil with methanol. By decomposing the organometallic complexes after reaction is completed they might be seperated from the glycerol şn order to have glycerol with higher purity. However there are some studies on biodiesel synthesis by using ethanol this is economically nonsense.

Ethanol is much more expensive than the methanol. Only environmental friendly character of ethanol makes us think about it but by the way if we consider that methanol is generally a unwanted byproduct of several reactions we can see that using methanol is also environmental friendly.

The simple transesterification reaction is as in below:

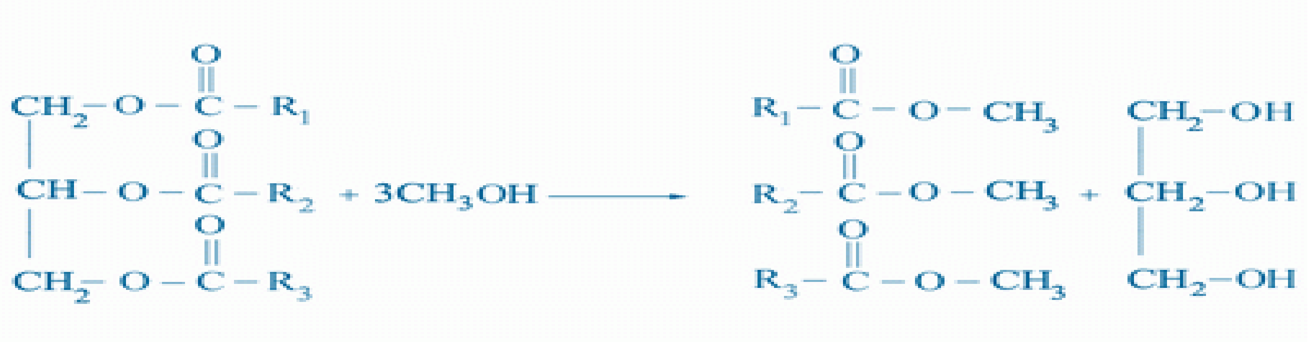

Fig 1: Transesterification reaction

As it is seen above methanol to oil ratio is 3:1 stoichiometrically.

Upto date transesterification reaction was performed with different methods as convectional heating, microwaves and ultrasonic irradiation etc. The only common industrial method is the one using conventional heating and agitation. Other methods are considerably new and are being researched now.

Using mercury light in order to produce a radical assisted reaction medium might give better yields in shorter times or even may give different byproducts. A very suitable method based on ultrasound is also being used. Carmen Stavarache, Mircea Vinatoru et al improved a method of transesterification of triglycerides to methyl esters by means of ultrasonic energy. As ultrasound is a very different type of energy application that is also used in emulsifying immiscible liquids. Methanol and triglycerides are immiscible liquids. By applying ultrasound they can be easily emulsified and by cavitation bubbles, a very high temperature and pressure reaction medium can be obtained (within the bubbles). Ultrasonic method seems to be a very feasible method. When ultrasound is used there is no need for a stirrer. Mixing (emulsification here) is caused by microscobic cavitation bubbles, a better emulsion can be obtained by ultrasound. Fabio Alape Benitez from University of Porto Rico states that ultrasound is a better heat application via convectional heating, it also gives better yields. Ultrasound in a higher frequency can also be used for phase seperation for seperating methyl esters and glycerol phases. This lowers the seperation time, yields high quality glycerol and biodiesel.

According to these datas ultrasound itself seems to be adequate for industrial biodiesel production. But there is a problem for finding large scale ultrasound crystals...

An idea of using microwaves and ultrasound can also be improved. The results can only be seen by performing the experiment then. Professor Kaddouri from Lyon University, France states that there is no need of stirring the components in the reactr after they are once emulsified, he also states that very high yields even upto 100 % were obtained by microwaves however the stirrer was not strong enough to emulsify the mixture. If we consider that ultrasound is a quite good emulsifier, microwaves are quite fast processors; the method seems to be a very fast and high yielding method. But this process type can result strange byproducts, the actual result can be understood by proving the experiment.

Feedstock:

The most important problem in industrial scale biodiesel production is the lack of oil feedstock. However it is mediatically stated that biodiesel can be produced from frying oil, there are very big burdens of that. First of all it is a quite big problem to collect fried oil, a properly working collection net is hard and expensive to establish. On the other hand kitchen use oil is not enough for high scale industrial needs. The other big problem is a chemical problem; fried oil includes moisture and too much amount of free fatty acids. Moisture causes saponification instead of transesterification. To get rid of this moisture extra energy and time is needed, that means extra costs. Frying oil also includes high percentages of free fatty acids. These free fatty acids also cause soap formation with alkali catalyst, so acidic catalysis must be used. We know that acid catalysts give lower yields within even a very long reaction time upto 40-80 hours; this makes too much energy, extra time loss, extra costs.. Maybe refining the used kitchen oil can be a solution to these problems, it is obvious that a refinery means spending more money.

Oils like virgin fat, canola oil, palm oil, sunflower oil and cotton seed oil can also be used as biodiesel feedstock. But most of countries have need to these oils, many countries import these oils. Oil farming for biodiesel feedstock must be done. If in future we are going to use biodiesel instead of diesel fuel; feedsocks available today will nor be enough for even a small percentage of worlds need.

Catalysts:

The most common catalysts used in biodiesel production are alkaline hydroxides as NaOH and KOH. NaOH is a very common chemical named as caustic soda and it is used in all chemistry related industries widely. KOH (sudcaustic soda) can always be used instead of NaOH by resulting almost the same yields. KOH is more expensive than the NaOH but it can be used in order to obtain K3PO4 , which is a good and valuable fertilizer. Ba(OH)2 can also be used. It was stated in our experiments that Ba(OH)2.8H2O gives about 90 % yields by convectional heating, where NaOH gives 95 % yield at the same conditions. As Ba(OH)2 is a heterogeneous catalyst, it is easier to seperate it from glycerol and reuse. By this way glycerol can be obtained with quite higher purity. This means more income.

Organometallic catalysts acting as NaOH, KOH or Ba(OH)2 mihgt also be used. This itself is a reseacrh topic. Ca(OH)2 is also a cheap heterogeneous catalyst but with lower yields.

There is also an acid catalysed biodiesel production process. This process gives better yields in presence of free fatty acids. While alkali based catalysts do not work with cooking oil, acid catalysts do work. Acid based catalysis also does not mind presence of moisture. The process must be performed in high temperature (~60 C), pressure and a long reaction time (~69 hours). Still the yields are generally less than 90 %. HzSO4 (aq) (98 %) is the most common acid catalyst used in biodiesel production. There is no information about acid catalysed biodiesel synthesis in presence of ultrasound. It must also be studied.

Supercritical methanol method needs no catalyst while methanol-oil ratio is extremely high (~500:1), high temperature (~300 C) and pressure is also high. There is also a seperation problem in this method because that high amount of methanol can dissolve the products. Distillation is necessary and this costs a lot.

Saponification:

Saponification is a very common chemical reaction based on combining alkali metals to fatty acids. It is a rapid reaction working with high yields. The reaction mechanism is as in below:

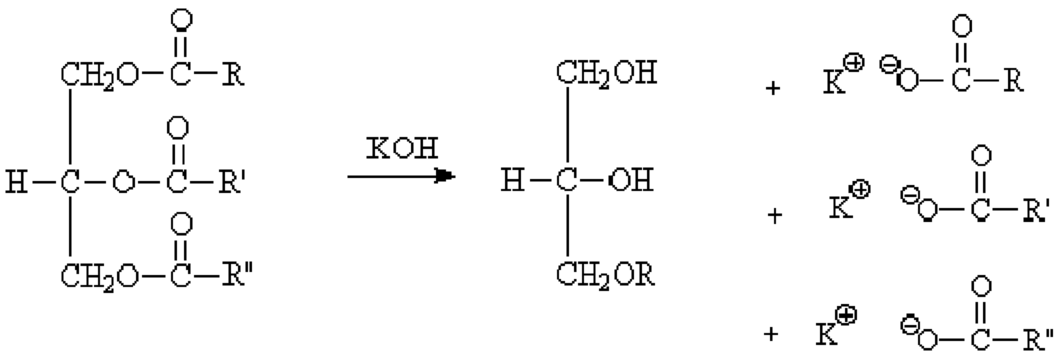

Fig 2: Saponification reaction

Seperation:

The products of the reaction are methyl esters of glycerides and glycerol. In order to determine the NaOH existence between phases, pnenolphtalein is used. The experiments show that NaOH passes to glycerol phase. Glycerol phase also includes the excess methanol. The complete phase seperation of the emulsion takes about 8 hours or longer due to the case. Centrifuge can be used in order to decrease this time. The density of glycerol is higher than that of biodiesel , and it is also very viscose. These features can help seperation by centrifuge or sedimentation. Because of being polar, NaOH and methanol dissolve in glycerol phase. Their solubility in biodiesel is very low. Soap formation increases the phase transfer and makes the phase seperation difficult. The soap places between biodiesel and glycerol phases. Biodiesels viscosity is very low in comparison to oil or glycerol. So it can be taken by pipeting. As it still can include impurities as alkali, methanol, glycerol, soap, it must be washed with water. The washing is repeated 2-3 times by dilute salty water and water is decanted off. To the obtained biodiesel with high purity, quality tests are applied.

The glycerol phase is heated upto 65 C in order to take the excess methanol in it. The methanol is distilled and collected in order to reuse. Glycerol then still includes NaOH in it. In order to purify it, the glycerol phase is first neutralised (if KOH is used as base , H3PO4 is used for neutralising it in order to obtain K3PO4) and distilled than. Glycerol is a valuable chemical that has a wide use area range.

Pyrolysis:

Pyrolisis is a biodiesel production method based on thermal cracking of triglycerides into smaller molecules. Pyrolysis is a process working on high temperature (~600 C) and high pressure. By pyrolysis not only biodiesel, but also gasolinelike molecules do form. As no unwanted compounds or catalyst wastes are present, no seperation problem occurs. Gasoline and biodiesel seperation is done by refining.

Lipase Catalysed Biodiesel Formation:

By using lipase enzymes, triglycerides can be converted to biodiesel. This method does not mind presence of moisture, but is a very slow and expensive method.

Results and Discussion:

Biodiesel is a feasible alternative energy source with environment friendly features. But as feedstock for biodiesel production is limited it is not a enogh good alternative to solve the whole energy problem. Availibility of biodiesel can be increased by making new improvements in agriculture of oil seeds.

Fast and high yielding techniques like microwaves or ultrasonic irradiation must be commonized in biodiesel production. Analytical tests must be applied to the product in order to understand the purity of the product. To improve the quality new and high technologies must be used. Transesterification seems to be the best way of obtaining biodiesel.

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