

ALTERNATIVE FUEL FOR INTERNAL COMBUSTION ENGINES. BIODIESEL, TRANSESTERIFICATION OF ANIMAL FATS WITH HIGH FFA

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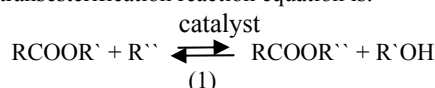
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ABSTRACT: This paper presents one method to obtain the ecological fuel “biodiesel” thru animal fats transesterification with high free fatty acid content. All tests were successfully made by the author at T.U. München. The method is presented step by step, including samples pictures.

Keywords: animal fat, biodiesel, liquid biofuels.

1 GENERAL ASPECTS

Transesterification is the general term used to describe the important class of organic reaction where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process the transesterification is called alcoholysis. The general transesterification reaction equation is:



Thus, it is obvious that the transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the pressure of the catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

Several aspects, including the type of catalyst (alkaline or acid), alcohol/fat molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification.

1.1 Acid catalysed processes

Sulphonic or sulphuric acids catalyse the transesterification process. The alcohol/fat molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favours the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/fat (oil) ratio has to be established empirically, considering each individual process.

Fatty acid methyl esters can be transformed into a lot of useful chemicals, and raw materials for further synthesis. The alkanolamides, whose production consumes the major part of the methyl esters produced in the world, have a direct application as non-ionic surfactants, emulsifying, thickening and plastifying agents, etc. The fatty alcohols are applied as pharmaceuticals and cosmetics additives (C₁₆-C₁₈), as well as lubricants and plastifying agents (C₆-C₁₂), depending on the length of their carbon chain.

1.2 Fatty acid ester as biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of this century. Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils and animal fats are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel. The physical characteristics of fatty acid ester (biodiesel) resulted in the end of the transesterification are very close to those of diesel fuel and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation.

2 Biodiesel experiments

In this paragraph the properties of the eleven old fats sample provided by the same manufacturer will be presented. It may be interesting to mention that the fats were originally produced to be used as a food in animal farms. The qualities of the fats are below the current norms (for animal use GROFOR-norm is active), and that is a very good reason and argument to try to use the fats for bio-diesel production. Measurements have been made for: iodine number (DGF-Methoden C-V 11b), sulfuric ash (DIN 51 575), total contamination (DIN 51419-A), peroxide number, kinematic viscosity (DIN 51 562 part 1) and free fatty acid (DIN 51 558 part 1). In figures 1, 2, 3 and Table 1 some pictures taken during the experiments and a synthesis of the old fat properties are given.



Figure 1: Determination of sulfuric ash



Figure 2: Determination of total contamination



Figure 3: Determination of free fatty acid: *left* – before titration, *right* – after titration.

Table I: Properties of fats

Sample	Iodine number	Acid number	Total contamination [mg/kg]	Viscosity [mm ² /s]	Sulfuric ash [%]	FFA [%]	Peroxide number
Jan 2001	64,76	21,63	12227	44,136	0,6839	10,87	58,4
Jan/Feb 2001	66,12	23,56	10709	43,084	0,4328	11,85	2,9
19.02.01	69,7	16,59	12028	43,264	0,4344	8,34	9,1
06.03.01	66	17,93	9385	42,666	0,3332	9,02	1,5
27.03.01	58,7	19,51	10598	49,592	0,3674	9,8	177,8
Apr 01	61	27,89	9026	41,373	0,3465	14,02	146,1
15.05.01	57	41,59	11050	49,59	0,6218	20,91	116,9
07.06.01	61	37,58	7177	44,978	0,475	18,89	1,4
21.06.01	53,4	32,84	9351	46,278	0,4934	16,5	13,3
06.07.01	66,7	29,99	6243	41,819	0,2988	15,08	28,9
23.07.01	58,9	22,3	7426	43,569	0,3715	11,21	14,5

According to the GROFOR-norm the fats with FFA over 15 % and total contamination over 5000 mg/kg are not suitable (red line in graphics) for use as food for

animals. So, it can only be used in industry (for soap, pharmaceuticals, lubricants products, etc.) or for bio-diesel production, as fuel for the internal combustion engines.

3 Biodiesel production tests

The authors tested two different methods to produce bio-diesel: *the first* is in accordance to the European patent application 0 249 463 A2 and *the other* is a similar method found on line in the Internet and updated by the research team. As only the last one has being successful, one will concentrate only on this one.

This is a two-stage procedure, acid first-stage and base second-stage. It is based on the highest free fatty acid (FFA) content found in used cooking oil, but it can be used with any waste vegetable/animal oil or fat, whether or not it has a high FFA content.

Fats preparation

The fat must be heated until it becomes liquid and then might be filtered. Two stages (acid-catalyzed stage and base-catalyst stage) should be accomplished.

For a successful reaction the oil must be free of water. There are two common methods of removing the water content:

Boiling the water off: heating to 100°C. As the heat raises the water, it separates out and falls to the bottom. The water is then drained out to avoid steam explosion. The temperature (> 100 °C) should be maintained until no bubbles are rising any more.

Settling the water out: This method saves energy. The fats must be heated to 60 °C and to keep this temperature for 15 minutes. After this one pours the fats into a settling tank and lets it settle for at least 24 hours. The water will separate and fall to the bottom.

The following strategy/receipt must then be fulfilled, step-by-step, for accomplishing successfully the fats preparation.

3.1 First stage (acid-catalyzed stage)

1. Measuring the volume of oil/fats to be processed (preferably in liters).

2. Heating the oil/fats to 55 °C -- all solid fats must be melted.

3. Measure out the methanol and provide 0.1 liter of methanol for each liter of oil/fats (10 % by volume). Add the methanol to the heated oil.

4. Mixing for 5 minutes; so the mixture will become murky because of solvent change (methanol is a polar compound, oil is strongly non-polar and a suspension will occur).

5. Adding for each liter of oil/fats the quantity of 1 milliliter of 95-97 % sulfuric acid (H₂SO₄). A graduated eyedropper, a graduated syringe or a pipette should be used. Special TAKE CARE when handling the concentrated sulfuric acid!

6. Mixing gently at low rotation speed (rpm), while keeping the temperature at 55 deg C. The rotation of the stirrer should not exceed 500 to 600 rpm, as speed is not crucial and splashed oil is a mess to clean.

7. Maintaining the temperature at 55 deg C for 50 minutes then stop heating. Continuing stirring.

8. Preparation of the sodium methoxide that consists of adding 0.1 liter of methanol for each liter of oil/fat (10 % by volume) and 3.1 grams of 99 % pure sodium lye

(NaOH) per liter of oil/fat. Finally mixing the lye into the methanol until the lye is completely dissolved.

10. Pouring half of the prepared methoxide into the mixture after 1.5 hours (oils only or oils plus fats) or 2 hours (for fats that are solid at room temperature). This will stop the acid-catalyzed reaction and prevent ester back splitting. Mixing for 5 more minutes, then stop.

11. Allowance to the mixture to settle for 6 to 12 hours, then draining off the glycerin. (the brown or dark brown compound at the bottom).

3.2 Second stage (base-catalyzed stage)

12. Heating the mixture to 55 deg C. Make sure that any remaining room-temperature solid fats are melted.

13. Adding the second half of the prepared sodium methoxide to the heated mixture and start mixing at the same low speed of not more than 500 to 600 rpm. Mix for 1 hour.

13. Allow settling for 6 to 12 hours.

14. Drain off the glycerin. The bio-diesel is now obtained.

3.3 Final stage (washing out the biodiesel)

For washing the pH of the FAME (fatty acid methyl ester) should be known.

The receipt comprises the following steps: Put the FAME in one vessel with ½ water or the same quantity of water as the FAME to wash. The FAME and water most have the same temperature (room temperature). The water pH must have as many units under 7 as the FAME's pH is above 7. Use strong vinegar to obtain lower pH for water. Use compressed air to create bubbles in the vessel ho contains the FAME/water mixture. Let it bubble for up to 6 hours. The bubbles will carry the water up. When this water falls down again, it washes the soaps and surplus methanol out of the FAME and the vinegar neutralizes the remaining lye. After settling for 12 hours the water will fall to the bottom, turning completely white and the bio-diesel will look much lighter in color now (Figure 3).

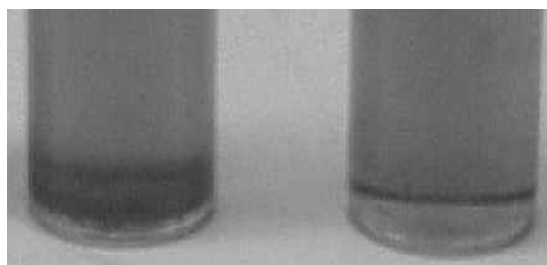


Figure 3: Biodiesel sample before (left) and after washing (right)

In Table 2 are presented the chemicals (CH₃OH – methanol, H₂SO₄ – sulfuric acid, NaOH – sodium hydroxide, KOH – potassium hydroxide) and their values used in the tests for producing the bio-diesel.

Table II: Properties of fats

Test No.	Fats [ml]	CH ₃ OH [ml]	H ₂ SO ₄ [ml]	NaOH [g]	CH ₃ OH [ml]	stage I [h]	stage II [h]	KOH [g]	CH ₃ OH [g]	Reaction time [min]
1	500	50	0,5	3,5	50	2	1			
2	500	50	1	3,5	50	2	1			
3	500	50	1	5	50	2	1			
4	500	60	1	4	50	5,3	1			
5	260	25	1	1	25	2	1			
6	250	40	2	1,5	40	2	1	2,53	26,35	25
7	250	40	2,5	2,65	40	2	1			

The most successful test was No. 6, realized with an extra step with KOH. The viscosity of the bio-diesel obtained was 5,3 mm²/s. Also the test No.7 was a partial success.

It should be mentioned that for the last step (KOH) for No. 6 it was used just 188,28 g collected at the end of the second step. Figure 4 is a view over samples from bio-diesel No.6. Note the lighter color and no depositions. Figure 5 is a general view over the biodiesel production process.



Figure 4: Probe No. 6 after second step(left), after third step with KOH (middle) and after washing (right)



Figure 5: Making Biodiesel

5 References

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4 Conclusions

As it is known the crude oil world reserves will not last forever and it is necessary to obtain alternatives fuels for piston engines. Another aspect is the more decent impact of these fuels on the environment. The search for alternative fuels is on wide spread in all developed countries.

The advantage of *bio-diesel* as alternative fuel relies first of all on its physical proprieties, similar with Diesel fuel proprieties so that bio-diesel can be use directly in Diesel engines with no essential modification of these. Second advantage is a very low impact on environment, and the third advantage is the accessibility of the breeding materials like old animal fats and a large variety of vegetable oils.

The tests described above are a real success and a step forward in developing new alternative fuels for piston engines.

4 Acknowledgement

The test have been accomplished in the frame of several projects of the hosts, the Technical University of Munich, Lehrstuhl für Energie- und Umwelttechnik der Lebensmittelindustrie, aslo with the financial support of the *Alexander von Humboldt* Foundation, for which deep thanks are expressed.