Acid catalysed transesterification of animal waste fat

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Abstract: Rendering plant fat (RPF) was collected and different conditions were used for transesterification. The course of transesterification of RPF was compared with that of transesterification of lard under the same conditions. Significant differences were found between transesterification of RPF and that of lard. Optimum methanol excess for lard transesterification was found to be 30-fold, for RPF 10-fold, optimum sulfuric acid concentration was 1% for lard, 2.5% for RPF. Optimum temperature as well as optimum reaction time were similar in both cases. The fatty acid composition is similar but not identical in both fats. RPF contains a higher amount of free acid which could be the reason for the differences observed.

Keywords: animal fat; animal waste; biofuel; rendering plant; transesterification

Oil reserves are still relatively large and new deposits are probably to be opened. Nevertheless, the availability of oil is decreasing as the needs for oil are growing too fast. Many new sources of energy are being developed and recommended for use, but most of them are inoperable (like wind energy or solar energy) or decline the availability of food sources (like bio-diesel or bio-ethanol) (see e.g. Stein 2007). Unfortunately, bio-ethanol and bio-diesel are the only chance for transportation after the oil era, while all other energy needs will be satisfied by nuclear power stations.

The landfill expenses are steadily growing which leads to the necessity of maximum utilisation of all wastes. Bio-diesel is usually produced by transesterification of soy oil (Muniyappa *et al*. 1996), palm oil (Carter *et al*. 2007; Stein 2007), rice bran oil (Zullaikah *et al*. 2005), but also from oil of defective coffee beans (Oliveira *et al*. 2008). These plant oils are then lacking in groceries.

The competition between food and fuel leads to the utilisation of different waste fats as the source material for transesterification. In fact, the last mentioned source, the defective coffee beans, belongs to this kind. Unfortunately, the amount of coffee beans available is not high enough for the large scale production. The utilization of the used cooking oil from restaurants for transesterification is another way to get fuel for transportation (Canakci 2007). But again, the quantity is low and the costs of collection are certainly not negligible. The cultivation of *Rhodotorula glutinis* (Feiyan *et al*. 2006) in cultivation broth after the fermentative production of glutamate can be an attractive source of raw material for transesterification when the cost of petrol is at least twice the actual cost.

As a consequence, we focused our attention on the fat material which is no source of food, is cheap and available in sufficient amounts. This material is the waste fat from rendering plants. It is readily available in relatively large quantities (300 000 tones annually in the Czech Republic, for instance), is concentrated in a small number of plants, and is cheap (in fact, the source-plants pay for ecological removal).

MATERIAL AND METHODS

Rendering plant fat (RPF) was obtained from the plant Agris Ltd., Medlov, the Czech Republic. RPF in this plant is separated mainly from pork and beef carcasses together with small quantities of other animal fats. Fat bodies are hacked to the pieces of 5 cm in diameter and heated 20 minutes to 135°C at the pressure of 0.3 MPa. The pressure is then lowered to allow the evaporation of all water. Finally, the grease is separated by the pressure of 30 MPa at 80°C. RPF is liquid at the

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beginning and is solidified at lower temperatures. The temperature of solidification is usually 40–50°C.

Lard was obtained from the Czech Agricultural University in Prague.

Transesterification was carried-out in 500 ml round-bottom flasks under reflux. 5 g of fat was dispersed in an appropriate volume of methanol in the presence of sulfuric acid and heated to the selected temperature for the selected time. The reaction was stopped by cooling in ice-cold water. Two layers are formed by this way. The lower layer consists of the un-reacted fat, sulfuric acid, and glycerol. The upper layer contains transesterified fat and methanol. The upper layer was then separated and distilled-off. Methylesters were extracted with diethylether for analytical purposes. The extract was then washed repeatedly with water to remove methanol and sulfuric acid residues and finally dried with dry sodium sulfate. Diethylether was then distilled-off at 30°C and dry methylesters were considered as the rough measure of the transesterification yield. The accurate yield was determined with the use of GLC. GLC determination of methylesters was carried-out according to the method described by Bannon *et al.* (1985). The conditions were: SPLIT T = 240°C, detector: FID T = 280°C; column: DB-23 (60 m, 0.25 mm, 0.25 μm, nitrogen flow rate 0.8 ml/min, 30°C).

Hewlett-Packard chromatograph model 6890N was used for GLC.

RESULTS AND DISCUSSION

The theoretical yield of transesterification was calculated from the fat composition. The amount of methylesters was 808 mg from 1 g of RPF. The theoretical yield for the transesterification of lard was determined to be 964 mg/g of lard.

Fatty acid compositions of RPF and lard are summarised in Table 1.

Acid catalysed transesterification begins with the addition of proton to the ester oxygen atom which forms more reactive electrophile. Next step is nucleophilic attack with free alcohol (methanol in our case) which forms tetrahedral intermediate in which both alcohols, the original one (glycerol) and that from the solution (methanol) are bound to oxygen. One of these alcohols is then liberated into solution. The product equilibrium depends on the relative reactivity of both alcohols and, of course, on their relative concentrations. Different courses of the reaction were found with RPF and lard. While lard reached optimum excess of methanol at 30-fold excess, RPF showed a constant decrease from 10-fold excess of methanol. These results are demonstrated in Figure 1. The acid catalysed reaction depends to a certain extent on the concentration of the catalysing acid. In our experiments, we measured the influence of sulfuric acid in the concentration range from 1 to 5%. The results are demonstrated in Figure 2.

Fat (glycerol ester) reacts in acidic media with free alcohol (methanol) as the counterpart while in the case of free acid, the counterpart is water. In such case a higher concentration of acid is necessary, as it serves also as the dehydrating component. One of the differences between RPF and lard is that RPF contains higher levels of free acids which are esterified (not transesterified) during the process. This

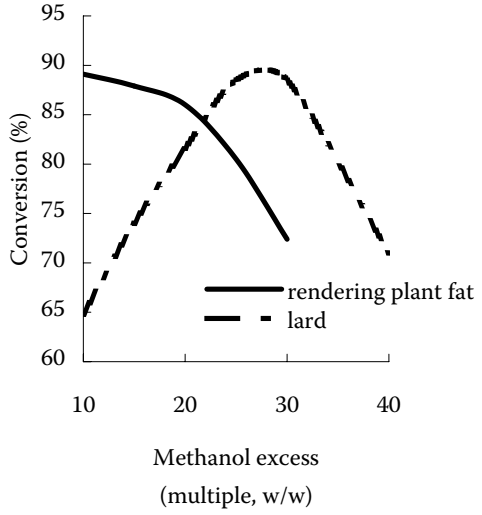

Figure 1. The influence of methanol excess in transesterification of rendering plant fat (RPF) and lard; reaction conditions: temperature 95°C, sulfuric acid concentration 1%, reaction time 7 h; full line – RPF

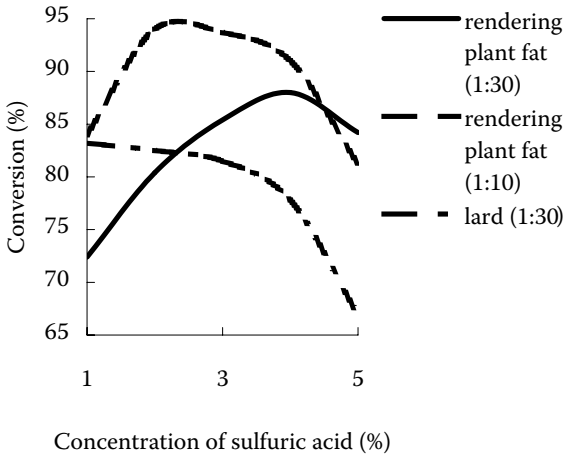

Figure 2. The influence of sulfuric acid concentration in transesterification of rendering plant fat (RPF) and lard; reaction conditions: temperature 95°C, methanol excess lard 30-fold, RPF10 10-fold, RPF30 – 30-fold, reaction time 7 h

Table 1. Comparison of the fatty acid composition in rendering plant fat and in lard

Fatty acid	Acid type	Fatty acid (%)	
		rendering plant fat	lard
Caprylic	C8	0.35	0.15
Caprinic	C10	0.07	9.00
Lauric	C12	0.10	0.09
Myristic	C14	1.06	1.58
Myristo-oleic	C14:1	0.13	0.02
	C15	0.12	0.06
Palmitic	C16	21.87	28.30
Palmito-oleic	C16:1	3.53	1.32
	C17	0.36	0.39
	C17:1	0.26	
Stearic	C18	10.10	18.01
Oleic	C18:1n9c	40.10	38.87
γ-linolenic	C18:3n6	0.60	0.02
α-linolenic	C18:3n3	1.38	0.36
	C18:4	0.12	
	C20	0.18	0.30
	C20:1n9	0.72	
	C20:2	0.34	
	C20:3n6	0.13	
Arachidonic	C20:4n6	0.32	
Eruic	C22:1n9	0.03	
Eicosapentaenoic	C20:5n3	0.03	
Docosahexaenoic	C22:6n3	0.09	0.14

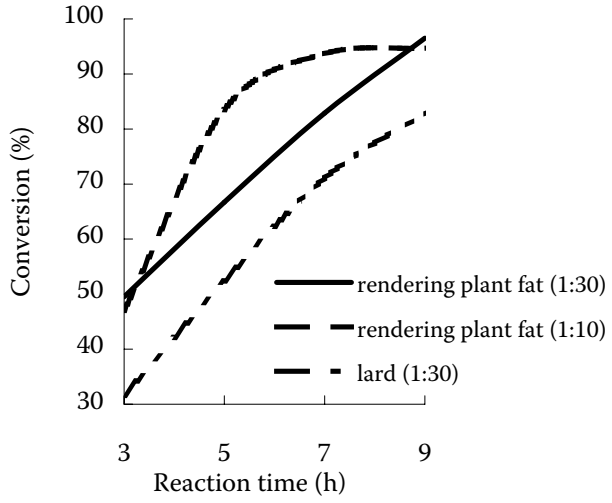

Figure 3. The influence of the time course on transesterification of rendering plant fat (RPF) and lard; reaction conditions: temperature 95°C, sulfuric acid concentration 1%, methanol excess 10-fold and 30-fold for RPF and 30-fold for lard

could be the explanation for the different reaction courses of RPF and lard.

An other important factor is the reaction time. The reaction proceeds to equilibrium given by the individual reactivities of the components. The reaction time, as a consequence, must exist in which the yield is maximum and does not grow any further. We monitored the dependence of conversion on the time of reaction in the time range from 3 to 9 hours. This dependence is shown in Figure 3. Again, the reaction courses of RPF and lard differ significantly. RPF transesterification in most favourable conditions (10-fold excess of methanol) gives a higher conversion in a shorter time as compared with that of lard.

The last factor affecting the reaction course of RPF is the reaction temperature. In general, higher temperatures increase the reaction rate, but do not

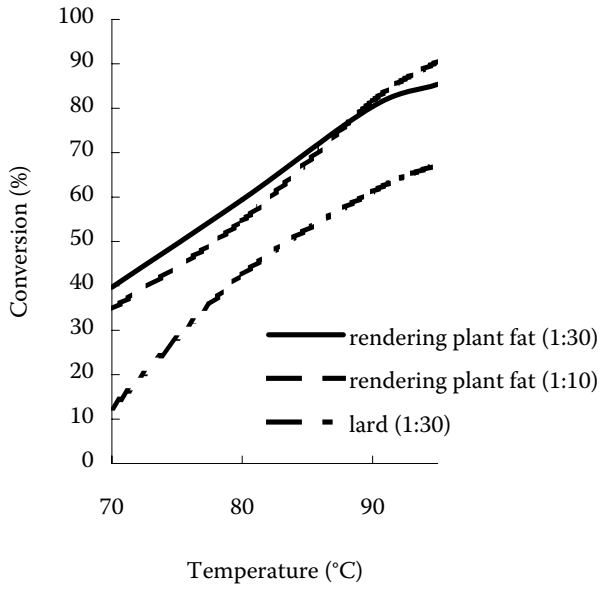

Figure 4. The influence of temperature on transesterification of rendering plant fat (RPF) and lard; reaction conditions: sulfuric acid concentration 1%, methanol excess 10-fold and 30-fold for RPF and 30-fold for lard, reaction time 7 h

influence the equilibrium. The temperature dependence of transesterification of RPF and lard under the optimums of other parameters is shown in Figure 4. Again, in optimum conditions RPF gives a higher conversion as compared with lard.

CONCLUSION

As a conclusion, rendering plant fat was found as a very suitable raw material for biofuel production according to the data given above. Fats saved for a longer time have in general higher contents of free acids (Zullaikah *et al*. 2005). RPF used in our work contains, according to the laboratory of the producer (Agris Ltd. Medlov, CR), approx. 32% of free acid. This fact could be the cause of the higher conversion of RPF as compared with lard and, at the same time, of the need of a higher concentration of sulfuric acid and a lower methanol excess.

Rendering plant fat may be considered as a new and advantageous raw material for the biodiesel production.

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Abstrakt

Prošková A., Kopicová Z., Kučera J., Škarková L. (2009): **Kysele katalyzovaná transesterifikace odpadního živočišného tuku.** Res. Agr. Eng., **55**: 24–28.

Sebraný kafilerní tuk byl testován z hlediska různých podmínek transesterifikační reakce. Průběh reakce tohoto tuku byl srovnáván s transesterifikací vepřového sádla za stejných pomínek a byly zjištěny výrazné rozdíly mezi průběhem transesterifikace u obou tuků. Optimální přebytek metanolu pro transesterifikaci sádla byl třicetinásobný, pro kafilerní tuk desetinásobný, optimální koncentrace kyseliny sírové byla 1 % pro sádlo, 2.5 % pro kafilerní tuk. Optimální teplota stejně jako optimální doba reakce byly podobné v obou případech. Složení mastných kyselin je pro oba tuky

podobné, ale nikoliv identické. Kafilerní tuk obsahuje větší množství volných kyselin, což může být příčinou zjištěných rozdílů.

Klíčová slova: živočišný tuk; živočišné odpady; kafilerie; transesterifikace

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