Possibility of Using Tannery Waste for Biodiesel Production**

by

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Abstract

Waste fat produced by tanneries during the processes in which raw hide is transformed into leather represents a very important raw material for biodiesel production. Under laboratory and pilot-scale conditions, biodiesel samples were prepared from waste tannery fat and required analyses were carried out. The process of biodiesel production has three stages: 1) refining melting of the raw material (separation of fats from other undesirable components), 2) organic base-catalyzed methanolysis and 3) separation of glycerin layer. The mathematical model of zonal refining melting is presented in this paper as well as the results of the refining and methanolysis product analyses. The use of organic bases (tetramethylammonium hydroxide, n-butylamine, cyclohexylamine, etc.) is innovative. It enables us, in addition to considerable financial benefits, to produce a high quality biodiesel and glycerin containing practically no ash. Further, it contains a residual amine that works as a stabilizer, and after methanolysis the amine can be partially recycled.

Resumen

Desperdicios conteniendo grasas producidos por curtiembres durante la transformación de piel al cuero son una importante material prima en la producción de combustibles biodiesel. Bajo condiciones de laboratorio y a escala de planta piloto, muestras de biodiesel fueron obtenidas de los desperdicios grasos de la curtiembre y los requeridos análisis fueron efectuados. El proceso de fabricación del biodiesel puede dividirse en tres etapas: 1) Refinación de la materia prima derretida (separación de la grasa de las materias no deseadas). 2) Metanólisis por medio de base orgánica y 3) separación de la capa conteniendo la glicerina. El modelo matemático para el refinamiento por zona derretida se presenta en esta obra como también los resultados del refinamiento y los análisis del producto de metanólisis. El empleo de bases orgánicas (hidróxido de tetrametilamonio, n-butilamina, cíclohexilamina, etc. es innovador. Nos permite, adicionalmente a los considerables beneficios económicos, producir biodiesel de alta calidad y glicerina prácticamente libre de ceniza. Más aún, contiene una amina residual que obra como un estabilizante, que luego de la metanólisis, la amina puede ser parcialmente reciclada.

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INTRODUCTION

Soy biodiesel is predominantly used in the United States, while canola biodiesel is dominant in Europe. The high price of biodiesel (over double the price of diesel) mostly results from the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, yellow grease and tannery fat wastes[1-3], which are unpleasant wastes and are consequently incinerated. The incineration is charged, which makes the tannery waste economically profitable in biodiesel production. The named other feedstocks need additional processing at the end of transesterification[1] to achieve required biodiesel properties, and would benefit from processing before transesterification to reduce or eliminate components that may affect final properties. In addition to plant oils, two animal feedstocks are included in biodiesel production – beef tallow and pork lard produced as tannery wastes[3,4]. The advantages of tallow and lard are their lower costs compared to soybean and canola oils. However, a disadvantage is that they may require additional processing to produce acceptable biodiesel[4]. To reduce this disadvantage we have worked out innovative technology which concerns removal of free fatty acids by their esterification. The esterification reaction is not catalyzed by strong inorganic acids, which is commonly used technology so far[3]. In our case, we used for esterification of free fatty acids tetramethylammonium hydroxide (TMAH). The excess TMAH acts as catalyst for the consequent transesterification reaction. This method of esterification of free fatty acids and transesterification of the respective triglycerides (oils, fats) has not been published according to our comprehensive literature review.

Chemically, biodiesel is a mixture of mono-alkyl esters of saturated or unsaturated higher fatty acids. The feedstock is animal fat and vegetable oils, in which the fatty acids are present in the form of triglycerides. Vegetable oils consist mostly of triglycerides of unsaturated fatty acids, while in animal fats predominate saturated fatty acids. The main chemical reaction in biodiesel production is alkali-catalyzed reesterification of glycerin esters of higher fatty acids by methyl alcohol to the respective methyl esters of the said acids, glycerin being released in the process. The alkali acts as catalyst and remains unchanged after the reaction is finished, while in fat saponification it is involved in the reaction as the respective fatty acid soap. The saponification is limited by the optimal concentration of the alkali catalyst.

Our contribution deals with the biodiesel production from waste tannery fat. We worked with waste fat from the TAREX-Otrokovice beam-house situated near our university. This fat is normally incinerated in a nearby factory.

THEORY

To make the waste tannery fat usable for biodiesel production, it is necessary to remove water, reduce the ash content and, if possible, to reduce free acid content (acid number). The above mentioned components make the content of the waste tannery fat. To reduce these components, we applied the refining melting process. First, the fat is heated to the melting point. Due to the low value of melting point (about 50°C) of the waste fat, we can use the waste heat from a dryer. The general mathematical-physical model of the process is represented by the following equations:

$$\frac{\partial t}{\partial \tau}(\tau,\hat{x}) = a\Delta_{(\hat{x})}t(\tau,\hat{x}) \quad (1)$$

$$t(o,\hat{x}) = tp \quad (2)$$

$$t(\tau,\hat{x}) = to(\tau) \quad \text{for} \quad \hat{x} \leftarrow \partial\Omega \quad (3)$$

$$\dot{Q} = B\frac{d\ to(\tau)}{d\tau} + C\frac{\partial t}{\partial \hat{n}}(\tau,\hat{x}) \qquad \hat{x} \leftarrow \partial\Omega \quad (4)$$

$$B = V_0\rho_0 c_{p0} \quad \text{and} \quad C = \lambda S \quad (5)$$

where Eq.(1) describes non-stationary temperature field, $\Delta_{(\hat{x})}$ is Laplace operator transformed into the respective coordinates, Eq.(2) is the initial condition, Eq.(3) represents the border of the sample surface set, Eq.(4) describes the heat balance on the heated sample surface, $\hat{n}$ stands for the outer unit normal vector.

As an example of solution for the above mentioned general model, dimensionless non-stationary temperature field for a cylinder shape is presented:

$$T = \frac{t}{t_p} = 1 + \frac{1}{16} + \frac{A}{4} + \frac{R^2}{4A+2} + 2P\sum_{n=1}^{\infty}\frac{J_0(R\,q_n)\exp(-Fo\,q_n^2)}{q_n^3 A\,J_1(q_n) - q_n^2 J_0(q_n) + 2q_n J_1(q_n)} \quad (6)$$

where q_n are roots of the following equation

$$A\,J_0(q) + \frac{J_1(q)}{q} = 0 \quad (7)$$

and

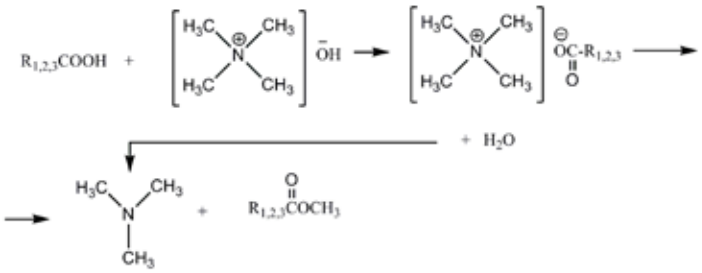
$$R = \frac{r}{b};\quad P\frac{\dot{Q}b^2}{2Vt_n\lambda};\quad A = \frac{aV_0 c_{p0}\rho_0}{2V\rho} \quad (8)$$

The liquid fat goes through filtration linen, while the solids (ash, proteins, etc.) are made into a filter cake. Filtrate cake can be either incinerated or pyrolyzed, the pyrolysis producing valuable components. The following Table I shows comparison of pyrolysis products of the filtrate cake and canola oil.

TABLE I
Products of filtrate cake and canola oil pyrolysis at 810°C

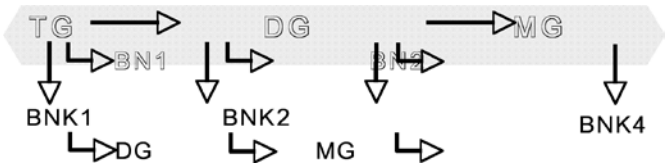
Component	BN-E1 34 (percentage by weight)	Canola oil (percentage by weight)
CO_x	-	-
Methane	10.1	6.5
Ethane	3.3	2.1
Ethylene	35.6	34.1
Propane	0.7	0.5
Propylene	12.7	13.5
Acetylene	0.6	0.7
iso - Butane	0.2	0.3
Propadiene	0.1	0.1
n - Butane	0.0	0.0
trans - 2 Butene	0.4	0.4
1- Butene	2.6	3.2
iso - Butene	0.2	0.2
cis - 2 Butene	0.3	0.3
Propyne	0.3	0.4
1,3 Butadiene	9.0	10.8
Cyclopentadiene + Isoprene	2.6	3.8
other C5-C6	2.5	3.1
Benzene	9.0	9.5
Toluene	3.4	3.4
Ethylbenzene	0.5	0.5
meta + para Xylene	0.3	0.4
Styrene	1.3	1.2
ortho Xylene	0.2	0.2
Naphthalene	0.6	0.6
other C7-C12	2.3	2.8
Oils	1.3	1.4

The next procedure depends on the content of free fatty acids. If the content is too high, it is necessary to implement their esterification. Most esterification processes are carried out in acid conditions and catalyzed by strong inorganic acids, for example sulfuric acid[1]. Another way is esterification under higher temperature (240°C) and pressure (9MPa)[5]. In our case, we carried out esterification of the free acids in alkali conditions by tetramethylammonium hydroxide (TMAH)[6,7]. The chemical mechanism of the process is as follows:

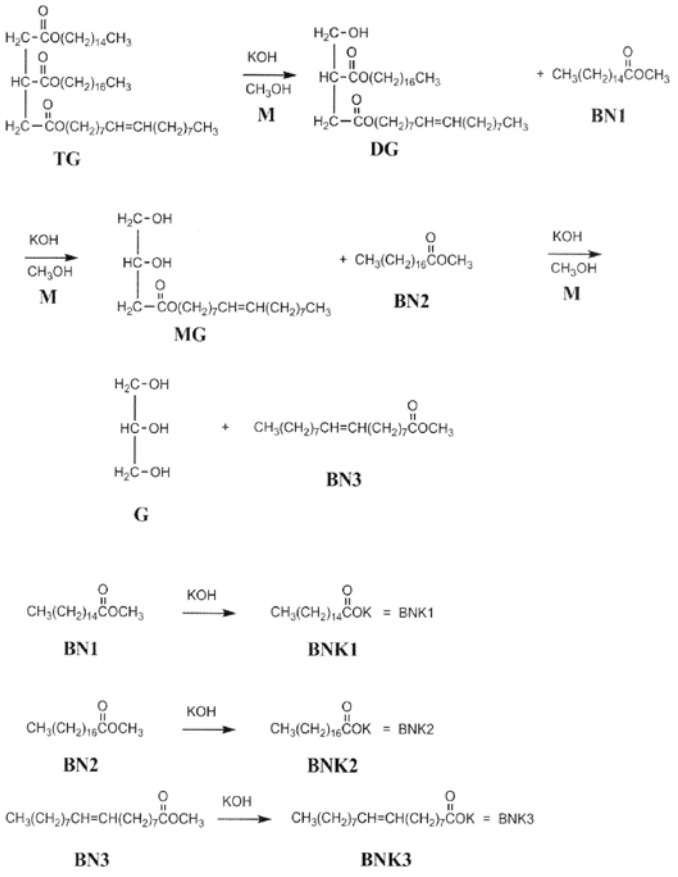


It is also possible to use other organic bases in the esterification reaction. We have tested several organic amines (for example butylamine, isopropylamine, ethanol amine) and the results are promising.

The main advantages of esterification in alkali conditions with the use of organic bases lie in the fact that no ballast inorganic salts are produced, high quality glycerin is obtained and the following fat reesterification by methanol can be performed immediately. Another appreciable advantage lies in the fact that the said volatile organic bases can be partially regenerated during the removal of the excess methyl alcohol by distillation. The whole chemical process can be simplified into the following scheme:



Detailed chemical reactions of the above stated scheme are the following:



EXPERIMENTAL

10 kg of waste fat were weighed out, placed into a linen sack and then put into a reheating furnace. The initial temperature was approximately 20°C and the liquefaction occurred at about 40°C (the melting point). At the same time, water steam was exhausted. The melting lasted 2 hours and 7 kg of the raffinate were obtained. The following Table II shows the composition of the raffinate in comparison with the composition of the feedstock before the refining process.

The table shows considerable decrease in ash content and a slight decrease in acidity number in the refined product. All the moisture was practically removed during the refining melting.

Reesterification in all samples was carried out in standard way. The reaction conditions were as follows: 100 g of waste fat, 100 g of methylalcohol, 1-5% of organic base (on the weight of the waste fat, according to the acid number), reaction temperature 60-70°C (depending on the boiling point of the reaction blend), and reaction time 2 hours. After reesterification, the excess methylalcohol was removed by distillation. Then the reaction blend was cooled and the glycerin phase was separated from the respective methylesters. The conversion of triglycerides into methylesters was estimated with the use of a chromatographic analysis. As an example we present the following diagrams (see Figures 1 and 2).

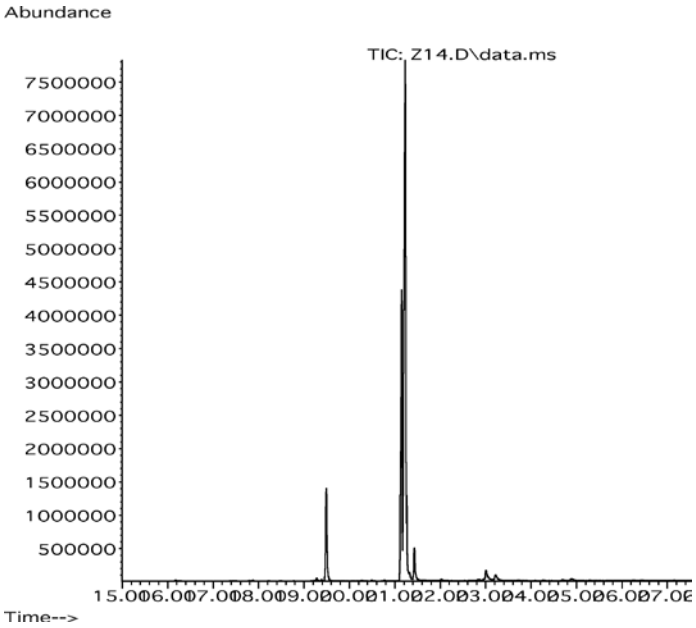


Figure 1: Sample BD1 - Total content of methylesters: 98.5 % (m/m).

TABLE II

Comparative composition of the fat refining products

	refined	non-refined
Volatile matter at 103°C (%)	undetected	27.26
Nitrogen (TKN)	undetected	undetected
Melting point (°C)	19.9	34.2
Ash (%)	0.16	1.05
Saponification number (mg KOH/g sample)	181.4	128.9
Acidity number (mg KOH/g sample)	10.6	13.3

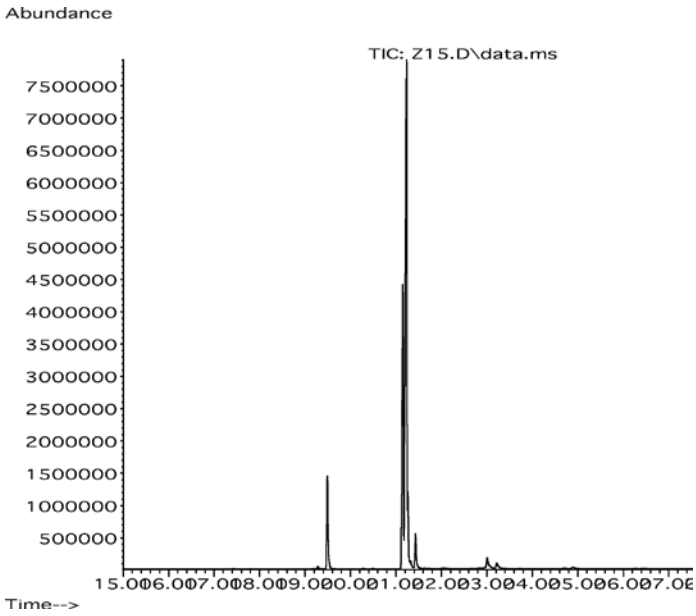


Figure 1: Sample BD2 - Total content of methylesters: 95.7 % (m/m).

Using tetramethylammonium hydroxide (TMAH) for esterification and as an alkali catalyst for reesterification has proved to be very utile. Commercially, TMAH is provided as 25% solution in methanol. A disadvantage of TMAH may be its price, which is probably high. For this reason, we have carried out with other organic bases such as N-butylamine, cyclohexylamine, isopropylamine, methylamine and diethylamine solution. Unfortunately, although their basicity is higher than in ammonia (pH of one molar solution is approximately 11.5), it does not reach the values of TMAH. One molar solution of TMAH reaches pH 14 (is totally dissociated like for instance KOH). For example, K_b of diethylamine[8] is 1.02×10^{-3}, which corresponds to pH 12.5 for one molar solution. Using the above mentioned substances individually has not been successful so far. Therefore, we used in both esterification and reesterification a blend of the above mentioned organic bases with potassium hydroxide (1-2% of KOH on the weight of the input fat feedstock). This resulted in a satisfactory separation of the methylester and glycerin layers. The use of KOH itself did not lead to such separation due to higher content of potassium soap. The mechanism of the organic base action probably is a chemical one, i.e. the organic base would act in a similar way like TMAH, resulting in the formation of gaseous ammonia at the boiling point temperature. We have examined this by heating a blend of 10% solution of stearic acid with N-butylamine at the boiling point and taking the outgoing gas into 0,1N sulfuric acid containing phenolphthalein. During two hours the sulfuric acid solution colored into red. From the known amount of neutralized sulfuric acid we calculated the respective conversion. The estimated chemical mechanism, like in the case of TMAH, may be described as follows:

$$RCOO^{-}H^{+} + R_1NH_2 \rightarrow RCOO^{-}NH^{3} + R_1 \rightarrow RCOOR_1 + NH_3$$

where $RCOO^{-}H^{+}$ is the acid waste animal fat and R_1NH_2 an organic amine (base)

Another possible mechanism of the organic base acting lies in a change of surface tension, which leads to the separation of the methylester and glycerin layers. This problem will be studied further and the results published.

DISCUSSION

If the transesterification of the acid waste tannery fat was carried out with only potassium hydroxide as a catalyst (1-2% of KOH on the weight of the input fat feedstock), then after distillation of the excess methanol we obtained a thick sticky mixture of mono-, di- and triglycerides, potassium soaps of fatty acids, from which the ester phase was impossible to be separated by standard methods. The conversion to methylesters was estimated to 40%, the yield 35%. We also carried out an experiment where we used 1:1 (by weight) blend of canola oil and refined fat from the tannery. The procedure was the same as described above. However, the conversion and yield did not improve. For comparison, we used commercial lard and plain canola oil as the input feedstock. The reaction was catalyzed by 1% (related to the feedstock weight) KOH. The content of free fatty acids, ash and moisture was negligible in this case. Both lard and plain canola oil feedstock gave a high conversion of 99.9% and there was no problem with the consequent separation of the methylester and glycerin layers.

Preliminary experiments with waste tannery fat containing free fatty acids (acid number 10.6) as feedstock and KOH as catalyst has proved inapplicable in biodiesel production. For this reason we approached the esterification of free fatty acids with tetramethylammonium hydroxide. Our work has proved that the waste tannery fat with high content of free fatty acids can be directly used for biodiesel production, i.e. with no previous acidic esterification, if we use tetramethylammonium hydroxide or a blend of organic bases with KOH.

CONCLUSIONS

Our current research has confirmed the possibility of using waste tannery fats in biodiesel production. Via refining melting it is possible to considerably decrease the content of water, ash, the acid number, or, possibly, the nitrogen content. For the esterification of free fatty acids it is beneficial to use alkali conditions achieved with the use of organic bases, e.g. TMAH (tetramethylammonium hydroxide). Some organic bases can be also used with promising results. In our case, we have tested cyclohexylamine, butylamine, isopropylamine and methylamine. The excess methylalcohol and the said organic bases can be re-distilled and reused in the reesterification reaction. On the basis of the present results of our research we assume that these results may contribute to a more efficient processing of other kinds of waste fat, e.g. yellow grease.

List of Symbols

t	Temperature	[K]
τ	Time	[s]
x	Coordinate	[1]
t_0	Surrounding temperature	[K]
V_0	Surrounding volume	[m^3]
ρ_0	Surrounding density	[$kg.m^{-3}$]
c_p0	Specific heat of the surrounding	[$J.kg^{-1}K^{-1}$]
$J_0(q)$	Bessel function of zero order	[1]
$J_1(q)$	Bessel function of the first order	[1]
λ	Thermal conductivity coefficient	[$W.m^{-1}K^{-1}$]
S	Surface of the heated sample	[m^2]
$\dot{Q}$	Thermal power of the heater	[W]
b	Sample thickness	[m]
V	Sample volume	[m^3]
t_p	Sample initial temperature	[K]
a	Thermal conductivity coefficient of the sample	[$m^2.s^{-1}$]

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REFERENCES

1. Tickell, J.; Biodiesel America 1st Ed., Yorkshire Press, Ashland, OH 44805, 2006.
2. Kinast, J.A.; Production of Biodiesel from Multiple Feedstocks and Properties of Biodiesels and Biodiesel/ Diesel blends, Gas Technology Institute, Des Plaines, Illinois, Final Report, NREL/SR-510-31460, 2003.
3. Çolak, S., Zengin, G., Ozgunay, H., Sarıkahya, H., Sarı, O. and Yuceer, L.; Utilisation of leather industry prefleshings in biodiesel production, *JALCA* **100,** 137–141, 2005.
4. Ma, F., Clements, L.D. and Hanna, M.A.; Biodiesel fuel from animal fat. Ancillary studies on transesterification of beef tallow. *Ind. Eng. Chem. Res.* **37**, 3768-3771, 1998.
5. Kreutzer, U.R.: Manufacture of fatty alcohols based on natural fats and oils. *J. Am. Oil Chem. Soc.* **61,** 343-348, 1984.
6. Lukes, R.: *Organic Chemistry,* Academia Praha, 1957. pp. 533.
7. Lawson, A.T. and Collie, J.N.; "XLVII. The Action of Heat on the Salts of Tetramethylammonium". *J. Chem. Soc.* **53**, 624 – 636, 1888.
8. Campbell, A.N. and Sing-Yeung Lam: "The dissociation constants and conductivities of mono-, di- and triethylamine in aqueous solution. *Can. J. Chem.* **51**, 551-555, 1973.