A Flexible Technology of Biodiesel Production from Fleshings

Karel Kolomaznik, Jiri Pecha, Vladimir Vasek, Michaela Barinova

Department of Automation and Control Engineering, Faculty of Applied Infrormatics, Tomas Bata University in Zlin.NadStrannemi 4511, 760 01 Zlin, Czech Republic

Abstract

Technology concerns an investigation of biodiesel (methyl esters) production from animal based feedstock in this case from fleshing. Fleshing need additional processing in order to achieve acceptable biodiesel properties and would benefit from processing before transesterification to reduce or eliminate components that may interfere with transesterification as free fatty acid, ash, protein and water. We have worked out pretreatment refining technology which includes desalinization, removal of protein, de-acidification and drainage processes. Additional investigation considered economic optimization with the goal to achieve refining cost lower than price of classical vegetable oils. Mathematical simulation using of theoretical tools of process engineering was used to achieve of named task. The final goal of our technology was to produce a fuel grade whose properties meet ASTM PS 121 standard or European standard of quality EN 14 214.

Keywords: Fleshigs, biodiesel, glycerin, gelatin, biostimulator, refining, economics.

1. Introduction

Besides the main product – leather – the tanning industry generates various by-products. One of promising usable by-product is fleshings as a feedstock for biodiesel production. The source for biodiesel is fleshings fat the content of which varies between 60-80%. However, the fleshings cannot be directly used for biodiesel production and for this reason a refining process is necessary.

The non-fat components of the fleshings are subcutaneous protein, salt and free fatty acids. The refining technology therefore comprises desalting, deproteinization and deacidification. The main total operating costs of the said processes must be lower than the prices of conventional feedstock for biodiesel production which is vegetable oil. For optimization of individual refining processes we used theoretical tools of chemical engineering in connection with the theory of transport phenomena. The optimization lies in determination of the target economical functions and finding of their minima for the main operating costs.

2. Theory

2. 1. Desalting

The salt present in the fleshings is removed by washing in pure water. Mathematical model of the desalting process is then the same as the model of raw hide soaking. Unlike soaking, the desalting of fleshings comprises only salt and therefore the mathematical model of desalting

is more adequate. The target function is then dependent on the consumption of electric power and the washing water. The following Table 1 and Fig. 1 represent the input data and the said function, respectively. The following function is based on the Second Fick`s Law. More details can be found in (Pecha et al. 2012).

Table 1 Example of the input data for optimization of desalting

ε	0,5	[1]	K_E	6	[CZK·kWh^{-1}]
D_e	10^{-9}	[m^2·s^{-1}]	K_V	60	[CZK·m^{-3}]
$2b$	0,005	[m]	m	5	[t]
P	20	[kW]			

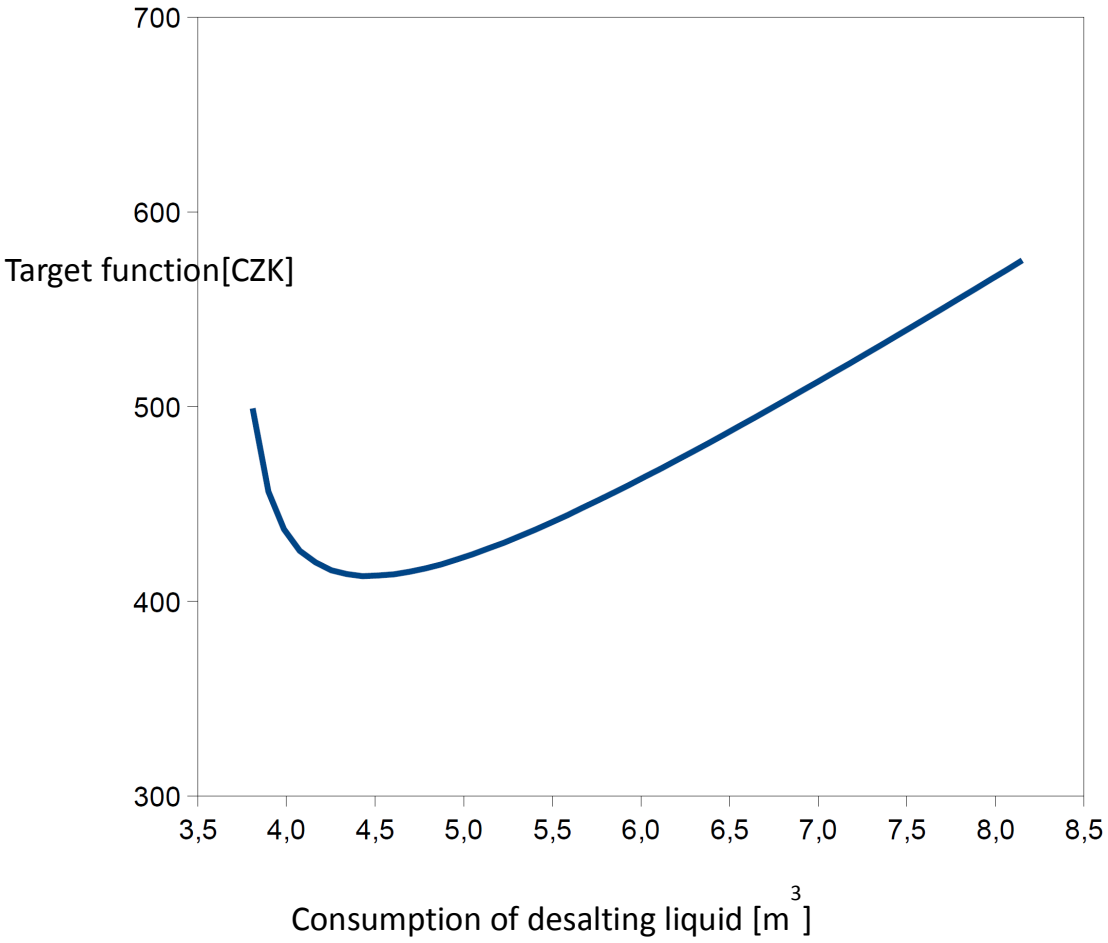

Fig. 1. Dependence of the main operating costs of desalting operation on the consumption of the desalting liquid.

2.2. Deproteinization

After removal of salt, the deproteinization is carried out at higher temperature which is given by the melting point of fleshings in hot water. The formed emulsion is then separated at cooling when the protein fraction goes to the aqueous phase. The aqueous phase contain high quality gelatin with average Bloom value of 200. The gelatin is then simply isolated by water evaporation. The high quality of the obtained gelatin significantly improves the economic aspects of the refining technology.

The mathematical model for deproteinization is simpler than the previous case because of the fact that the decelerating effect of transport phenomena is practically eliminated.

$$N_S = -\frac{K_E \cdot P}{k} \cdot \ln\left(1 - \frac{c_0}{c_{ro}}\right) + K_p \cdot (\Delta H)_{evap} \cdot Na \cdot V \cdot \left(1 - \frac{c_0}{c_K}\right) \cdot \rho \qquad (1)$$

The above mentioned target function includes the kinetics of deproteinization (k, c_0, c_{ro}, and c_K) and costs of water evaporation (K_p), besides the unit prices of electric power (K_E), water consumption (V, Na), the input power of electric motor (P) and the enthalpy of evaporation (ΔH_{evap}). The following Table 2 and Fig. 2 represent an example of the input data and the said function, respectively.

Table 2 Example of the input data for optimization of deproteinization

K_E	6	[CZK·kWh^{-1}]	ρ	1000	[kg m^{-3}]
K_p	600	[CZK·MJ^{-1}]	k	0.0143	[min^{-1}]
V	1	[m^3]	Na	5	[1]
P	5	[kW]	c_K	950	[kg m^{-3}]
$(\Delta H)_{evap}$	2.3	[MJ kg^{-1}]	c_0	900	[kg m^{-3}]
c_{ro}	150	[kg m^{-3}]			

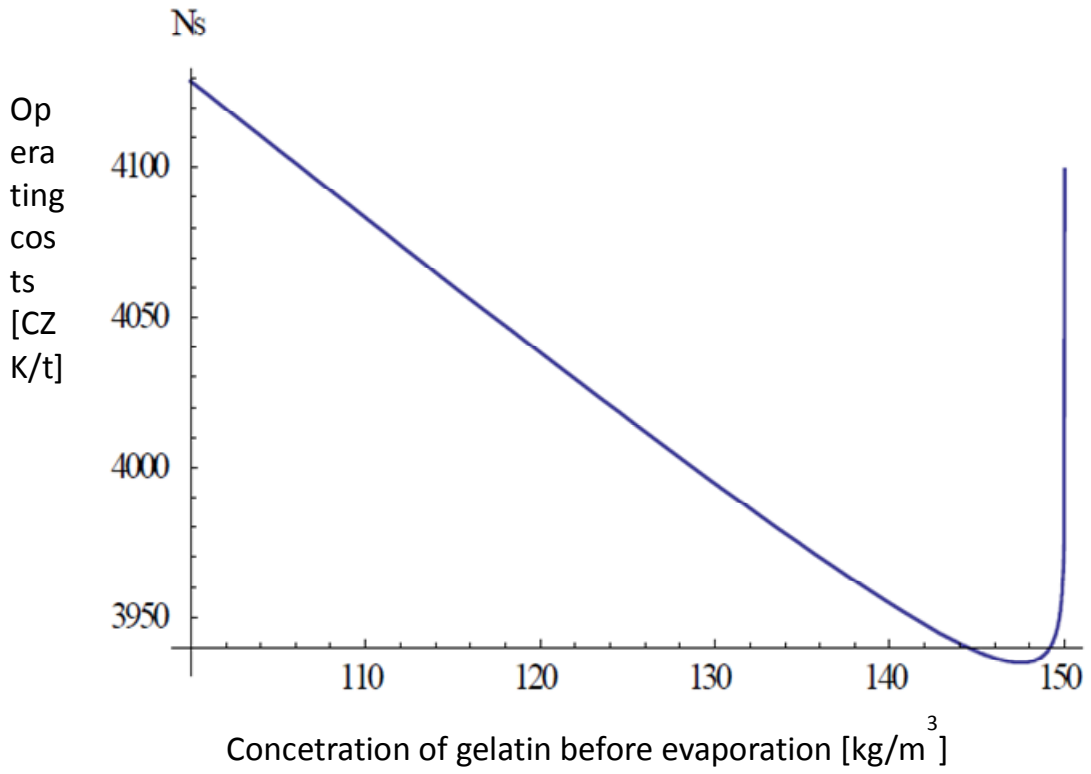

Fig. 2. Example of the dependence of the unit operating costs of deproteinization on the concentration of gelatin.

2.3. Deacidification

The acid value of fleshings usually exceeds 2 mg KOH/g. Therefore their direct processing via alkali –catalyzed transesterification is not suitable since the inorganic alkali catalyst (e.g. potassium hydroxide, sodium methanolate) is spent on free fatty acid neutralization and the conversion of the transesterification reaction is not high enough. Moreover, salts (soaps) formed during this reaction prevent easy separation of the methyl ester (biodiesel) and glycerin phase and simultaneously the formed water again decreases the transesterification yield. There are several methods how to solve the above described problem. Generally, it is possible to apply esterification reaction, but we apply an extraction processes. There are two main ways of extraction – physical and chemical. Both ways represent multi-component extraction of partly miscible phases. Chemical extraction involves using organic base solutions. The mathematical model is based on approximate mass balance. Final quantities of both phases and the content of substances in both phases are evaluated from experimentally measured partition coefficients and the amount and composition of the input feedstock. The partition coefficient is defined as a ratio of mass fraction of all substance in both phases.

2.4. Transesterification

Transesterification is a reaction during which the fat refined in the previous processes is converted into biodiesel, *i.e.* fatty acid methyl esters (FAME). This reaction is complicated since it is a system of three consecutive reactions which are reversible (see scheme in Fig. 3). As can be seen in the reaction scheme, in the first reaction the triglyceride (TG) is converted into a diglyceride (DG) and a methyl ester, next step similarly converts obtained diglyceride into a monoglyceride (MG) and another molecule of methyl ester, and finally in the last step glycerol is released from monoglyceride simultaneously with the third molecule of methyl ester. This mechanism is important for understanding the reaction and also for subsequent optimization of the reaction conditions.

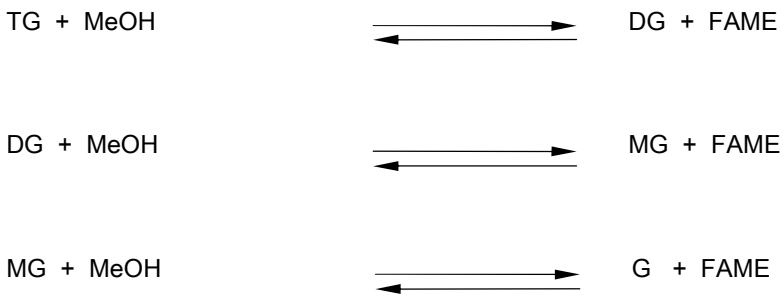

Fig. 3. Scheme of transesterification reaction.

If the final biodiesel is to meet the demanding international standards of quality (e.g. EN 14 214), the conversion of TG to FAME must be very high (higher than 98.8%). This requirement is based mainly on observations that higher amount of intermediates is harmful for diesel engines (Sanek et al. 2013).

The transesterification can be catalyzed by acids or bases. In industry, the base catalyzed processes are preferred namely due to their higher reaction rates compared to acid catalysis (Freedman et al. 1984). On the other hand, the base catalyzed reaction is more sensitive to feedstock impurities, such as water or free fatty acids. Consequently, the optimization of the refining processes and careful choice of reaction conditions is essential for ensuring the high quality of final biodiesel.

3. Experimental

One kilo of fleshings of the following composition (dry mater content 77% w/w, sodium chloride 5% w/w and nitrogen (TKN) 7% w/w), was mixed with one kilo of cold water and subjected to three cycles of decantation washing. About 80% of sodium chloride was removed. The rest of fleshing was drained, dried and melted, and the protein part (solid greaves) was separated by filtration. The separated protein was extracted by hot 80°C water and filtered to obtain water solution of gelatin which was concentrated and dried at laboratory temperature. Bloom value of gelatin was 150. The filter cake was treated enzymatically and the hydrolysate was tested as a biostimulator with positive results. Solid fleshing fat with acid number of 20 mg KOH/g was extracted with cyclohexylamine methanolic solution and the

total free fatty acid content was removed. The refined de-acidified flashing fat was treated with methanol and a mixture of tetramethylammonium hydroxide (TMAH) and isopropyl amine (ratio 1:10) and the re-esterification process took place at 70°C for 2 hours. The excess of methanol and isopropyl amine was distilled off and the biodiesel layer was separated from pure glycerin. The obtained biodiesel and glycerin were of the following composition: Biodiesel upper layer - 99.12% FAME (fatty acid methyl esters – biodiesel), MG (monoglycerin) 0.48%, DG (diglycerin) 0.04%, TG (triglycerin-fat) 0.33%, G (glycerin) 0.03%. Glycerin lower layer - G 69.93%, FAME 29.15%, MG 0.42% and TMAH 0.5%.

4. Conclusion

The flashings as a by-product of processes in which raw hide is transformed into leather is promising feedstock for the production of high quality biodiesel and glycerin. Moreover, production of gelatin with relatively high Bloom value and enzymatic hydrolysates improve the overall economic effect of complex processing of flashings into valuable products.

5. Acknowledgements

This work is supported by the Ministry of Education, Youth and Sports of the Czech Republic, by European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.

6. References

Freedman, B., Pryde, E. H., Mounts, T. L. Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils, *JAOCS*, 61(10), 1638-1643p.

Pecha, J., Kolomazník, K., Bařinová, M., Šánek, L., 2012, High Quality Biodiesel and Glycerin from Fleshings, JALCA, 107(10), 312-322p.

Sanek, L., Pecha, J., Kolomaznik, K., 2013, Simultaneous determination of main reaction components in the reaction mixture during biodiesel production. Journal of Separation Science, 36(6), 1029–1036p.