# Economic Aspects of Biodiesel Production from Tannery Waste Fats*

*by*

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## Abstract

The present high price for biodiesel results from the high prices of it's main feedstock—soybean (USA) and canola oil (Europe). The potential profit from the utilization of low cost tannery fat wastes for biodiesel production depends on the processing costs of the pre-treatment technology; which includes their refining and esterification of free fatty acids. A suitable ratio of tetramethylammonium hydroxide, which is used as an alkali esterification agent of free fatty acids and simultaneously as a transesterification catalyst, enables making biodiesel production from tannery waste feedstock economically profitable. Optimization of the pre-treatment technology is presented using a proposed mathematical model. The final biodiesel properties can be improved by its production from the blends of the waste fats with waste oils.

## Resumen

El presente alto precio del biodiesel resulta por los altos precios de su fuente principal-soja (USA) y aceite de canola (Europa). La ganancia potencial por la utilización de desperdicios grasos de curtiduría de bajo valor para la producción de biodiesel depende de los costos de la tecnología del pre-tratamiento; que incluye su refinación como también la esterificación de los ácidos grasos libres. Una proporción adecuada de hidróxido de tetrametílamonio, el cual se emplea como un agente de esterificación alcalino de los ácidos grasos, y simultáneamente como un catalizador de trans-esterificación, permite la fabricación de biodiesel más económicamente posible a partir de fuentes de desperdicios de tenería. La optimización del la tecnología del pre-tratamiento es presentada usando un propuesto modelo matemático. Las propiedades finales del biodiesel pueden mejorarse en su producción empleando mezclas de desperdicios de grasas con desperdicios de aceites.

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## INTRODUCTION

Tannery waste fats have high energetic content that is utilizable for production of heat, electric and volumetric power for diesel engine. There are several ways how to utilize their net calorific value:

- simple combustion; the produced heat is employed directly to the heating of e.g. buildings
- converting the gained heat energy to the production of electric power
- anaerobic fermentation; the produced methane may be stored and utilized as a pure fuel
- biodiesel production

The use of the above mentioned methods depend on particular technological and economic conditions that are available for their individual users. The key factor is the economy of waste tannery fat processing that is represented by the prices of energetic products. The net calorific value of pure fat is approximately 39 MJ/kg.[1] An average price of heat is 400 CZK/GJ which corresponds to 20 USD/GJ. Therefore, combustion of 1 kg of fat with 100% energy conversion efficiency earns 0.78 USD/kg. If the heat energy is used for electric power production with usual energy conversion efficiency (25%), 2.7 kWh of electric power is produced from 1 kg of waste fat. Hence, the earnings from the electric power are about 5 CZK/kWh (~0.25 USD/kWh), which corresponds to 0.675 USD/kg.

It is possible to made biogas from waste fats by their anaerobic fermentation according to equation (1).

$$C_{55}H_{104}O_6 + 26H_2O \longrightarrow 39CH_4 + 16CO_2 \qquad (1)$$

As can be seen, the obtained biogas is a mixture of carbon dioxide and methane; 1 kg of fat yields approximately 1 $m^3$ of pure methane which means income of 0.5 USD/kg of waste fat when we calculate the price of cubic meter of methane 10 CZK (~0.5 USD).

From 1 kg of waste fat it is possible to produce nearly 1 kg of biodiesel, i.e. 1.16 liters at the average density of 860 $kg/m^3$. The price of biodiesel is 40 CZK/l (~2 USD/l) assuming that the price of biodiesel is approximately twice as high as the price of diesel fuel.[2] Therefore, the income from 1 kg of waste fat is 2 USD.

Although the real market prices of the waste fats processing products may differ, their relative comparison clearly shows that from the economic point of view the most profitable way of waste fat utilization is biodiesel production. For this reason, we have focused on this technology in our research. From a chemical point of view, biodiesel is a mixture of methyl esters of long-chain fatty acids both saturated and unsaturated. Biodiesel is produced by transesterification of vegetable oils and animal fats with short chain alcohol, typically methanol. More precisely, main constituents of these lipids are triglycerides of long chain fatty acids and these are transesterified. Animal fats have higher content of saturated fatty acids in comparison with vegetable oils. Nowadays, the main feedstock for biodiesel production is vegetable oil – usually canola (EU) and soybean (USA). Since these oils are relatively expensive, more than 70% of the price of biodiesel is given by the price of this feedstock (see Fig 1).[3]

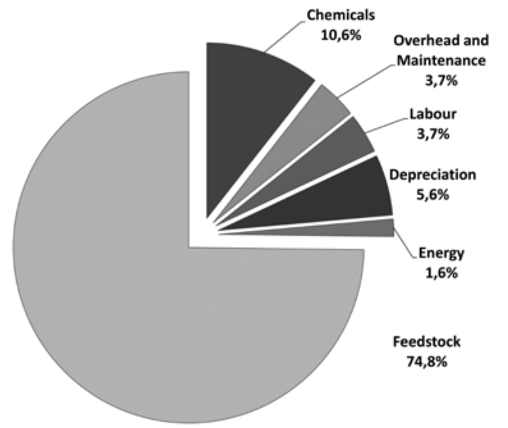


Figure 1: Typical costs composition of biodiesel production[3]

Nevertheless, biodiesel can be made from other feedstock. The most promising so far are raw waste fats and oils, the price of which is much lower than that of vegetable oils (sometimes even negative—their elimination is charged). Utilization of waste fats and oils also fits well in the requirements for renewable, sustainable and clean energy sources. In addition, biofuel crops in such case do not occupy the farmland. However, the advantage of low price of such feedstock is reduced by the need for their pre-treatment. Furthermore, there is a risk of the decreasing tendency of vegetable oil prices. These were quite high especially in 2007–8, copying the biofuel boom on markets, but more extensive biodiesel production and global economic crisis have led to their decrease.[4]

On the other hand, in 2007 in the USA a kilo of soybean oil cost 66 cents (660 USD per metric ton) while a kilo of waste poultry fat from food processing concerns cost 38 cents (380 USD per metric ton).[5] Therefore, the biodiesel production from waste fats is obviously economically promising. One of the promising sources of waste fats is tanning industry. Since fleshings (as the main waste fat produced by tanneries) usually have an acid value over 2 mg KOH/g, the classical biodiesel production route via alkali-catalyzed transesterification is not suitable for their processing because the inorganic alkali catalyst (e.g. potassium hydroxide, sodium methanolate) is spent on free fatty acids (FFA) neutralization. Moreover, salts formed during this reaction prevent easy separation of the methyl ester and glycerin phase; also water which is simultaneously formed with salts decrease the yields of the transesterification.[6,7,8] In addition, it was reported that a recommended acid value of the feedstock for alkali-catalyzed transesterification should be lower than 1mg KOH/g to achieve ester purity prescribed by American standard for commercial grade of biodiesel ASTM D6751.[9]

There are several methods that are capable to overcome the problem with FFA content in the low quality feedstock. Probably the most examined method is an acid-catalyzed esterification of FFA which is also used at an industrial scale,[10] in contrast to the majority of other techniques (e.g. enzymatic esterification and transesterification,[11] fat treatment in supercritical methanol[12]) which are rather in the phase of an intensive development.

In the acid-catalyzed esterification method a strong inorganic acid (like sulfuric acid) is employed as a catalyst for esterification of FFA to methyl esters. The esterification facilitates lowering of FFA content to a level at which an alkali catalyst may be employed for subsequent transesterification of acylglycerols.[13] The acid is able to catalyze also transesterification of acylglycerols, but this reaction is too slow;[8] thus, the above described two-step process is used in the industrial practice, the FFA esterification step serves as a pretreatment of the acid fat feedstock. It was reported recently that fleshings might be successfully processed to biodiesel with this technology to a purity which is nearly sufficient to fulfill the requirements prescribed by European standard for commercial grade of biodiesel EN 14 214.[14]

Canakci et al[15] published their experience with a scale-up of the two-step esterification technology in which sulfuric acid was employed as an esterification catalyst. It was necessary to conduct the pretreatment twice to obtain high conversion in the esterification. After the first esterification, the water-methanol phase was allowed to settle as long as 24 hours before it was removed from the once pretreated fat and the pretreatment was repeated. Then, the refined fat was transesterified with an inorganic alkali. The obtained ester layer was six times washed with water to fulfill the maximal total and free glycerol content prescribed by the ASTM standard. The overall ester yield was approximately 90%. The total costs of the produced biodiesel were calculated as 0.36 USD/kg, including the price of the feedstock. The biodiesel from yellow grease was about 24% cheaper than biodiesel made from soybean oil (the price comparison is valid for situation in the year of the paper publication).

Nevertheless, a few problems concerning the acid pretreatment technology were reported. The main drawback of the described technique is the necessity of acid neutralization prior to alkali transesterification which leads to a formation of large amounts of salts in the reaction system.[16] These salts must be removed from the final biodiesel (and also glycerin) which may be the limiting factor during the product purification.[17] Thus, much effort is made to develop suitable solid esterification catalysts (e.g. paper[16]) which are easily separable from the reaction mixture after successful esterification. Despite the fact that some of these solid catalysts are available commercially, the solid catalyst efficiency and its possible fouling are still an issue, namely in case of esterification under mild reaction conditions, i.e. at atmospheric pressure and temperatures around 60°C.[16,17,18]

Different approach was published in our previous paper.[19] Raw waste fat is pre-treated prior to its transesterification. One of our tasks is to optimize the proposed pre-treatment technology in relation to minimization of the main operation costs and to keep the advantage of substantially lower price of the feedstock. The pre-treatment technology includes:

- Mechanical removal of water content by pressing or centrifugation. The optimization suggestion lies in minimization of the energy necessary for pressing, eventually centrifugation. These processes are able to substantially reduce consumption of energy necessary for water evaporation in the next step.

- Programmed refining melting; it controls the heating of the refined fat to achieve removal of the protein and reduction of the ash content, and simultaneously determines the free fatty acid content and moisture removal.

- Decomposition of organic soaps (formed from FFA) to biodiesel and trimethylamine and alkylation of the latter substance to the original organic base. In the simplest case, trimethylamine is sold directly as a valuable product for chemical industry

The free fatty acids and triglycerides are converted to methyl esters (biodiesel) with the use of an organic base – tetramethylammonium hydroxide (TMAH), eventually this base is blended with volatile organic bases, namely alkylamines. TMAH has a dual role: it reacts with FFA giving salts of FFA and TMAH ("organic soaps") and its excess serves as a strong alkali catalyst during transesterification. Methanol is distilled of the obtained reaction mixture, the final distillation residue contains methylester and glycerin layers, the organic soaps are predominantly in the glycerin layer. When organic soaps are heated above 150°C, their decomposition takes place. The organic soaps are decomposed to methylesters of the respective fatty acids (i.e. biodiesel) and gaseous trimethylamine which is expelled from the reaction mixture (as its boiling point is only 3°C). This gas can be converted again to the original catalyst TMAH via its alkylation—such process facilitates regeneration of TMAH.

## THEORY

The purpose of the waste fat and oil pre-treatment is to achieve the feedstock quality comparable to that of pure vegetable oils. The economic viability of the biodiesel production process from waste fats and oils is determined by the costs of the pre-treatment processes. Hence, the total costs of the pretreatment (including the price of the waste fats) must be lower than the price of pure vegetable oils. This approach enables us to apply relatively simple mathematical models based on economic balance because it is not necessary to deal with transesterification process itself, which is not different from the common technology. The costs of water removal and refining melting are low (waste heat of tannery driers may be employed for this purpose) in comparison to the esterification of FFA. Thus, we presume that only costs of esterification together with price of the feedstock are substantial for the economic optimization of the pre-treatment technology.

The specific price of waste fats and oils ($n$) may be represented as a function of their free fatty acid content which is expressed as an acid value ($x$). It is possible to approximate the real data with the exponential cost function (Eq. 2).

$$n = A \cdot \exp(-B \cdot x) + C \qquad (2)$$

The price of the esterification agent is dependent on the actual feedstock acidity value, thus the overall operating costs ($y$) can be written as an expression (Eq. 3).

$$y = K_{OB} \cdot x + n \qquad (3)$$

According to our presumptions, the profit ($p$) is then equal to the difference between the price

of pure vegetable oil and the overall operating costs of waste fat pre-treatment (Eq. 4).

$$p = k - y \qquad (4)$$

The extrema ($X_{min,max}$) of the above stated functions (Eq. 3 and 4)—minimum of the overall operating costs and maximum of the profit—can be calculated from the following equation (Eq. 5).

$$X_{\min,\max} = \frac{-1}{B} \ln\left(\frac{K_{OB}}{A \cdot B}\right) \qquad (5)$$

There is a certain limiting factor of biodiesel production from waste animal fats—the cloud point of such biodiesel is higher than the cloud point of biodiesel made of vegetable feedstock. This is caused by the fact that the melting point of saturated fatty acid methyl esters is higher in comparison with the methyl esters of unsaturated fatty acids. The said disadvantage may be reduced by blending of waste animal fats with waste vegetable oils, such as used cooking oils. The key factor, again, is the economic viability of this method. It is therefore necessary to ensure that the overall operating costs of the pre-treatment procedure do not exceed the acceptable level. Since the tannery fat is at least on the Czech market free of charge (at current state), we may assume that the overall operating costs ($y$) are determined by the costs of esterification of FFA present in both waste tannery fat and waste vegetable oil, and the price of waste vegetable oil – ($n_O$), (see Eq. 6).

$$y = K_{OB}\left[x_{TF} \cdot a_{TF} + x_O \cdot (1 - a_{TF})\right] + (1 - a_{TF}) \cdot n_O \qquad (6)$$

## RESULTS AND DISCUSSIONS

The suggested feedstock cost function (Eq. 2) was used to fit the real data sets. We have compared a short U.S. market survey from paper[15] with the situation in the Czech Republic from our own survey. The fitted data sets are shown in Fig. 2.

As can be seen, the real market situation corresponds to its prediction by the model. Pure vegetable oil is substantially cheaper on the U.S. Market but the price of waste fat is high in comparison to the Czech market. This discrepancy may be attributed to the date of the USA survey—it was published in 2001, whereas Czech prices are from 2010. There is also another important aspect—the USA prices are the prices of the rendered waste fats (i.e. they are sold as final refined products), whereas the Czech data set contains prices obtained directly from the producers who sell the raw waste fats as their by-product. Furthermore, it is most probable that the acidic waste fats bought from resellers and renderers are notably more expensive (similarly as in the USA). The production of biodiesel, which includes *in situ* raw waste fat refining, is therefore more profitable.

Since the dependency of the feedstock price on its acid value is non-linear, the operating cost function (Eq. 3) and profit function (Eq. 4) have extrema. Figure 3 reveals their position on the Czech market.

As shown, the maximal profit over 0.60 USD/kg is obtained when the feedstock has acid value around 15mg KOH/g (the profit estimation is valid for the catalyst price 0.008 USD/ acid value). The calculations done for the U.S. market are less optimistic due to the higher prices of the feedstock, maximum profit reaches approximately 0.02 USD/kg in the case of the same input economical parameters. However, the current prices of pure soybean oil at U.S. market are approximately as twice high[20] as the calculated from the year

2001. Thus, the real current profit is more optimistic also on the U.S. market. Aside from the price of the waste fats and oils, the second important constituent of the overall operating costs is the price of the esterification agent. Its impact on the overall operating costs and consequently also the profits is clearly demonstrated in Fig. 4 and Fig. 5, respectively.

Since the esterification agent is consumed during FFA pretreatment, the maximal profit moves forward to the feedstock with lower acid value when the price of the organic base is increased. An optimal acidity value of the feedstock (which ensures maximal profit) plotted as a function of the alkylation agent price in Fig. reveals clearly this relation. Moreover, the

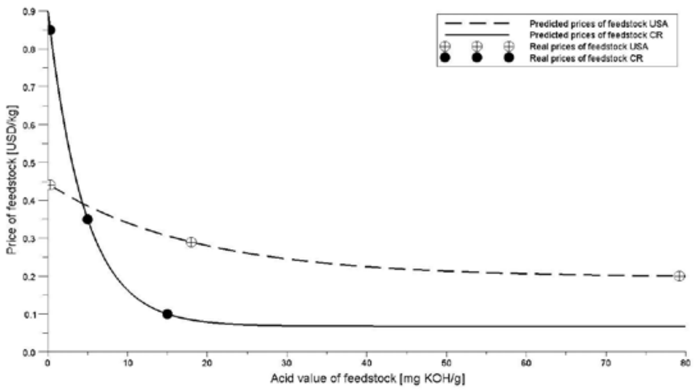


Figure 2: Dependency of prices of waste fats on their acid value

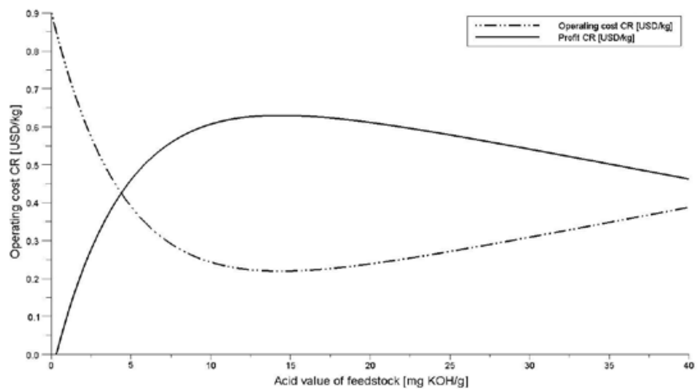


Figure 3: Estimated profit and operating costs as functions of feedstock acid value (Czech market)

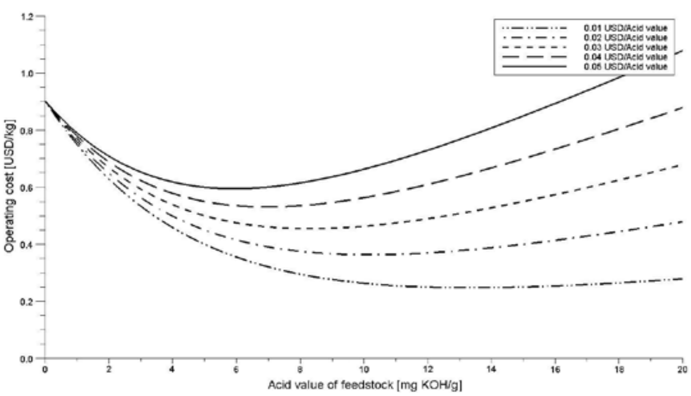


Figure 4: The influence of esterification system price on the overall operating costs (Czech market)

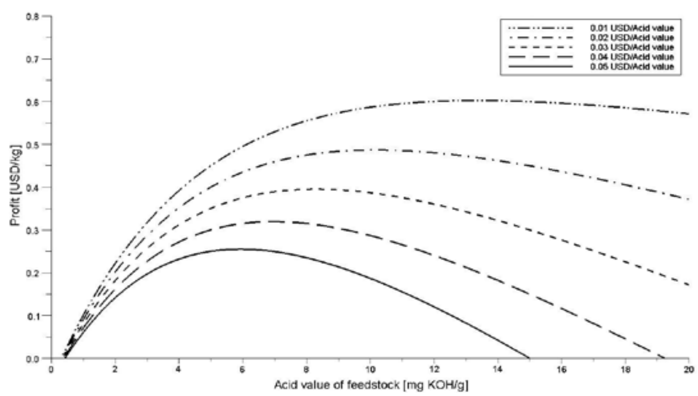


Figure 5: The influence of esterification system price on the profit (Czech market)

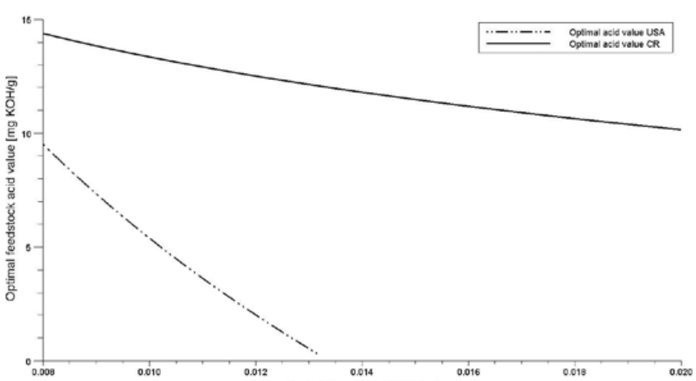


Figure 6: Evaluated optimal feedstock acid value and its dependency on the price of the catalytic system

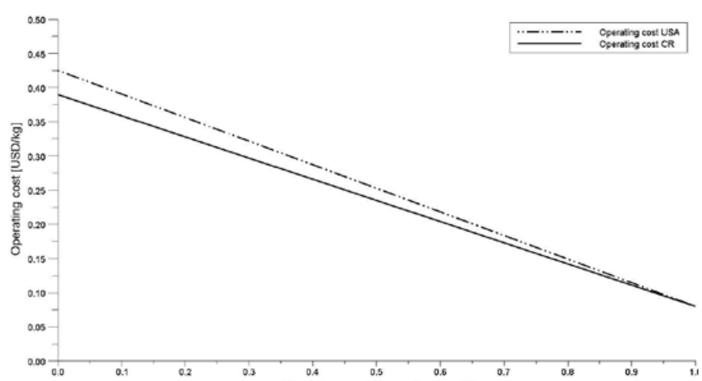


Figure 7: The overall operating costs of the waste oil and tannery waste fat blend

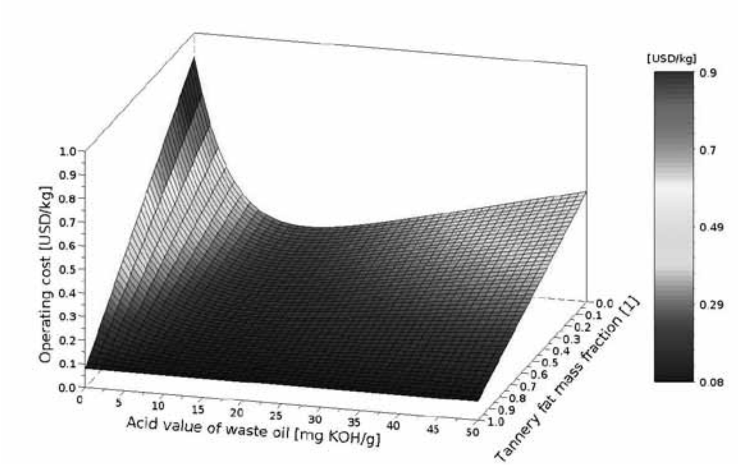


Figure 8: The overall operating costs as a function of waste oil acid value and feedstock blend composition

real range between the maximal and the minimal market price of the catalytic system seems to be quite large. The TMAH prices, which we have obtained from its producers, illustrate this issue well—the highest offer was more than 6 more expensive than the cheapest one.

As already stated above, blending animal waste fats with waste oils is advantageous from the final biodiesel properties point of view. We have evaluated the economy of this feedstock blend—the price of the resultant mixture, which is dependent on the blend composition. Calculations were done with a blend of animal fat with acid value 10mg KOH/g (representing the tannery waste fats) and waste oil with acid value 5 mg KOH/g (usual value of used cooking oils). Figure 7 describes estimated overall operating costs of the final blend. These costs are the lowest when pure tannery fat is used which is caused by our assumption that the price of raw tannery waste fat is negligible (which is true on the Czech market). Nevertheless, the price of the blend may be still competitive especially in comparison with the price of pure vegetable oil. The precise composition of the mixture is therefore a compromise between final biodiesel properties and feedstock costs.

However, the acid values of the feedstock often fluctuate in the reality. In such case an optimal composition can be found with the help of expression (Eq. 6). Figure 8 describes the overall operating costs dependent on the blend composition and waste oil acid value. As can be seen, the optimum lays in the range from acid value 10 to acid value 20mg KOH/g.

[Editor note: Figures 1 and 8 were originally in color. For color copies of these figures please contact the editor or the authors]

## CONCLUSION

The waste tannery fats (namely fleshings) are utilizable via several different technologies. The comparison between estimated prices of the final products of these technologies showed that the most profitable is waste tannery fat utilization in biodiesel production. It was demonstrated that the overall operating costs of biodiesel production from waste fats and oils can be estimated in a simple way as the costs for waste fats pre-treatment to a quality comparable to pure vegetable oils. This approach was employed for economical optimization of waste fats pre-treatment technology that uses organic bases as catalytic system. The optimization showed that there are two crucial factors. The first is the price of waste fats—the comparison between the Czech and U.S. markets indicate that

## LIST OF SYMBOLS

| | | |
|---|---|---|
| $a_{TF}$ | Mass fraction of the tannery waste fat | [1] |
| $A$ | Parameter of feedstock cost function | [USD/kg] |
| $B$ | Parameter of feedstock cost function | [g/mg KOH] |
| $C$ | Parameter of feedstock cost function | [USD/kg] |
| $k$ | Price of pure vegetable oil | [USD/kg] |
| $K_{OB}$ | Price of organic base catalyst/esterification agent | [USD/acid value] |
| $n$, $n_O$ | Specific price of the feedstock and waste oil, respectively | [USD/kg] |
| $p$ | Profit | [USD/kg] |
| $x$, $x_{TF}$, $x_O$ | Acid value of the feedstock, tannery fat and oil, respectively | [mg KOH/g] |
| $X_{min,max}$ | Extrema of the function | |
| $y$ | Overall operating costs | [USD/kg] |

Other symbols are explained directly in the text *in situ* raw waste fat refining is probably more profitable than using refined products provided by renderers and distributors. The second factor is the price of the esterification agent—there are large discrepancies between the offer of producers (and distributors). The influence of the latter factor on the suggested biodiesel production technology may be decreased by the regeneration of the alkylation agent. Since biodiesel made from animal fats has higher cloud point, blending animal feedstock with waste vegetable oils is advantageous from the technological point of view. The suggested mathematical approach allows estimation of the optimal composition of the mixture according to the feedstock acidity value and its price. Nevertheless, the real optimum is rather a compromise between the economic and technology optima that are usually different.

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