

CHROMATOGRAPHIC ASSESSMENT OF ROMANIAN TALL OILS FATTY ACIDS AS FEEDSTOCKS FOR BIODIESEL PRODUCTION

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Abstract: Biodiesel, as an alternative fuel for internal combustion engines, is defined as a mixture of monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock. A variety of biolipids can be used to produce biodiesel. These are: virgin vegetable oil feedstock (rapeseed, soybean, sunflower and palm oils); waste vegetable oil; animal fats; and non-edible oils such as tall oil, castor oil etc. Tall oil is a by-product of the manufacturing of pulp and paper products. It is one possible feedstock not commonly studied for biodiesel production. The amount and composition of fatty acids of tall oil depends on the processed pulpwood species. To our knowledge no study were found about fatty acids content of crude tall oil produced in Romania's pulp factories. The aim of the present work was the identification and

quantification of fatty acids as FAMES (fatty acid methyl esters) in crude tall oil samples from Someș-Dej (T₁) and Ambro-Suceava (T₂), using gas-chromatography (GC) with flame ionization detector (FID). The main fatty acids found in both studied tall oils were: linoleic, oleic and palmitic, acids at different concentrations, depending on the oil origin. It were observed that in sample T₂ the sum of percents of saturated fatty acids (10.22%) and monounsaturated fatty acids (48.27%) was higher then in sample T₁ (12.05% and 40.82% respectively) but in each of them these sums were higher then the total amounts of polyunsaturated fatty acids (T₁: 47.13% and T₂: 41.49% respectively). The high proportion of saturated and monounsaturated fatty acids is considered optimal from a fuel quality standpoint.

Key words: biodiesel, tall oil, fatty acids

INTRODUCTION

Biodiesel, defined as an alternative fuel composed of mono-alkyl esters of long-chain fatty acids (like lauric, palmitic, stearic, oleic, etc.) prepared from vegetable oils or animal fats, has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petrodiesel). (DEMIRBAS, 2009)

The interest in the use of renewable fuel started with the direct use of vegetable oils as a substitute for diesel. Vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources. Vegetable oils have the potential to replace a fraction of the petroleum distillates and petroleum-based petrochemicals in the near future (BHALE et al., 2009).

Chemically speaking, vegetable oils and animal fats are triglyceride molecules in which three fatty acid groups are esters attached to one glycerol molecule. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdoms that are made up of 1 mol of glycerol and three moles of fatty acids and are commonly referred to as triglycerides (MOSER, 2009). The conversion of vegetable oil into methyl esters through the transesterification process (oil or fat reacts with methanol or ethanol in the presence of a sodium hydroxide or potassium hydroxide catalyst) approximately reduces the molecular weight to one-third, reduces the viscosity by about one-seventh, reduces the flash point slightly

and increases the volatility marginally, and reduces pour point considerably. (HERNANDO et al., 2007).

A variety of biolipids can be used to produce biodiesel. These are: virgin vegetable oil feedstock (rapeseed, soybean, sunflower and palm oils); waste vegetable oil; animal fats; and non-edible oils such as tall oil, castor oil etc. The waste and inedible vegetable oils are easily available in developing countries and are very economical comparable to edible oils (DORADO et al., 2003a, 2003b).

Crude tall oil is a by-product in the manufacture of paper pulp by pulping processes. (BOKIS et al., 1999). It contains 40–50% resinic acids, 30–40% fatty acids and 10% neutral or unsaponifiable material (NOGUEIRA, 1996). Elemental analysis shows that tall oil contains 11.0% oxygen, 79.1% carbon and 9.9% hydrogen (SHARMA, BAKHSHI, 1991). Tall oil methyl ester–diesel fuel blends had the advantages of decreasing CO emissions (up to 38.9%), low sulphur content and higher cetane number (ALTIPARMAK et al., 2007). The chemical composition varies with the age, pine species, geographical location of the coniferous trees and pulping process (KESKIN et al., 2007). In Romania, the main resinous species are spruce, silver fir and pine (of 21.7%, 4.8% and 1.8% respectively, from total forestry area).

To our knowledge no study were found about fatty acids content of crude tall oil produced in Romania's pulp factories. The aim of the present work was the identification and quantification of fatty acids as FAMES (fatty acid methyl esters) in crude tall oil samples from Somes-Dej and Ambro-Suceava, using gas-chromatography (GC) with flame ionization detector (FID).

MATERIAL AND METHODS

Sampling and reagents

Crude tall oil samples T1 and T2 were obtained from the pulp and papermaking factories Somes-Dej and Ambro-Suceava (Romania), respectively.

Lipid standards were from Sigma-Aldrich (St. Louis, MO, and USA), Merck or Fluka (Buchs, Switzerland). All chemicals and solvents (analytical-reagent grade or HPLC grade) used were purchased from Merck (Darmstadt, Germany).

Sample preparation for fatty acids analysis

For total fatty acids analysis, FAMES (the more volatile forms of fatty acids) were prepared by transesterification of the oil samples by sodium methoxide (CH_3ONa) catalysis in anhydrous methanol (CH_3OH) (CHRISTIE, 1982).

The transesterification steps:

1. were weighed 30mg oil into a reaction vessel (Pyrex tube), containing 1ml of organic solvent (toluene)
2. were added 2ml from the reagent which was prepared by dissolving 0.4g CH_3ONa in 15 ml anhydrous methanol
3. was heated and kept at 70-80°C for 1 hour. Once the mixture has cooled to room temperature, were added 1ml water and 1ml hexane or petroleum ether after the phases were separated, the upper (organic) layer was carefully removed and dried on anhydrous sodium sulfate.

The dried organic phase was purified then by column chromatography. The column was packed with Silica gel 40 (0.063-0.200 mm) (Merck- Germany). The FAMES were eluted with petroleum ether: diethyl ether = 90:10(v/v) solvent mixtures. After the fractions were collected, the solvent mixtures were evaporated and the separated fractions were re-dissolved in hexane and submitted to GC analysis.

The experimental conditions

The FAMES were analyzed using a Shimadzu GC-17-A gas chromatograph equipped with FID and a 30 m Alltech AT-WAX coated with polyethylene glycol (0.25 mm I.D., 0.25 μ m film thickness) capillary column. The analysis conditions were: flow rate 1.8 ml/min, splitting ratio 1:20, flow gas helium, temperature of injector and detector 260^oC, temperature gradient 150^oC (5 minutes) and 4^oC/min gradient until 235^oC. The identification of the peaks was achieved by retention times and by comparing them with authentic standards analyzed under the same conditions. In addition, literature data on fatty acid GC retention properties, fatty acid compositions of various vegetable oils were used to assist peak identifications (BRODNJAK-VONCINA et al. 2005; LEE et al. 1998). The quantitative determination was performed by internal normalization using an ISO standard (ISO 5508:1990(E)).

Statistics

All the extractions and GC-FID analysis were made in triplicate. Results were expressed as mean \pm standard deviation (SD). Statistical differences between samples were tested using ANOVA (GraphPad Prism Version 4.0, Graph Pad Software Inc., San Diego CA) at a 95% confidence level.

RESULTS AND DISCUSSIONS

The fingerprints of the fatty acids (as FAMES) in studied tall oils are presented in Fig.

1.

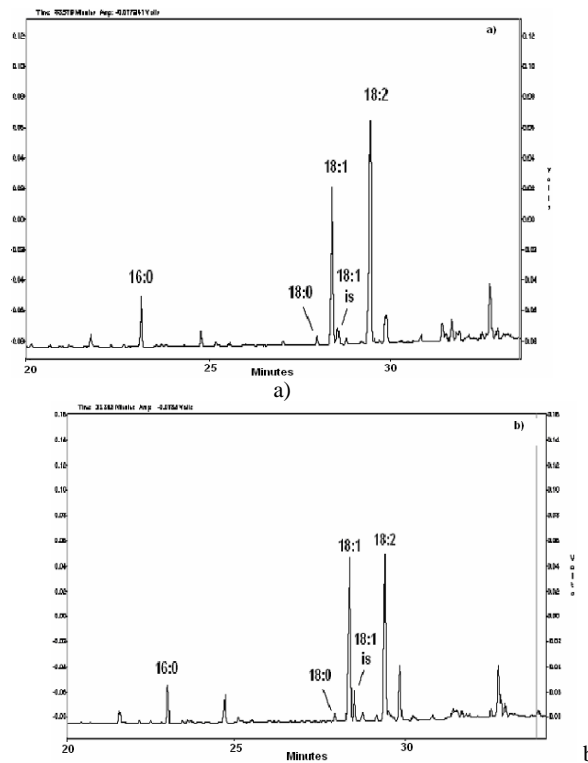


Figure 1: GC-FID chromatogram of total FAMES of Romanian crude tall oils: a) T₁- from Somes-Dej ; b) T₂- from Ambro-Suceava

Table 1. illustrates, the difference between fatty acid compositions of tall oil samples.

The main fatty acids found in both studied tall oils were: linoleic, oleic and palmitic, acids at different concentrations, depending on the oil origin.

Statistical analysis using T-test at $P < 0.05$, showed extremely significance differences between T_1 and T_2 for: palmitic acid (10.15% vs. 8.50%); oleic acid (36.98% vs. 42.20%); vaccenic acid (3.84% vs. 6.07%) and linoleic acid (47.13% vs. 41.49%).

The dates for studied two Romanian tall oils were compared to values reported in the literature, summarized in the Table 2.

There was some difference in the fatty acid distribution in T_1 and T_2 found in the present study and by other researchers. ALTIPARMAK et al. (2007) and KESKIN et al. (2007) found a much higher average level of oleic acid in Turkish tall oils (52.7% and 50.2% respectively) compared to our results and those of YORDANOV et al. (2008) (T_1 : 36.98%- T_2 : 42.2% and 38% respectively).

There was also a discrepancy in the palmitic, stearic and linoleic acid concentrations of tall oils in this study compared to that of YORDANOV et al. (2008) (Table 2).

Crude tall oil T_1 from Somes-Dej had higher concentrations of SFA (12.05%) and PUFA (47.13%) than tall oil T_2 from Ambro-Suceava (10.22% and 41.49% respectively). It were observed that in sample T_2 the sum of percents of SFA (10.22%) and MUFA (48.27%) was higher then in sample T_1 (12.05% and 40.82% respectively) but in each of them these sums were higher then the total amounts of polyunsaturated fatty acids (T_1 : 47.13% and T_2 : 41.49% respectively). The high proportion of saturated and monounsaturated fatty acids is considered optimal from a fuel quality standpoint in that fuel polymerization during combustion would be substantially less than what would occur with polyunsaturated fatty-acid-derived fuel.

Table 1

The fatty acid compositions (weight %) of Romanian tall oils							
Fatty acid composition (% of total fatty acids)							
Fatty acids	Abbr.	T_1		T_2		R_i (min.)	T test ($P < 0.05$)
		Mean	SD (n=3)	Mean	SD (n=3)		
Palmitic	16:0	10.15	0.18	8.50	0.12	23.06	***
Stearic	18:0	1.90	0.09	1.72	0.10	27.95	ns (p=0.0814)
Oleic	18:1	36.98	0.32	42.20	0.31	28.38	***
Vaccenic	18:1is	3.84	0.12	6.07	0.18	28.53	***
Linoleic	18:2(ω-6)	47.13	0.36	41.49	0.38	29.43	***
Total(%)		100.00	1.07	99.98	1.09		
Σ SFA		12.05	0.27	10.22	0.22		***
Σ UFA		87.95	0.80	89.76	0.87		ns (P=0.0568)
UFA/ SFA		7.30		8.78			
Σ MUFA		40.82	0.44	48.27	0.49		***
Σ PUFA		47.13	0.36	41.49	0.38		***
PUFA / MUFA		1.15		0.86			

Results are mean of three replicate analyses.

T_1 and T_2 , tall oil samples; Abbr., abbreviation; R_i , (min.), retention time (minutes); SD, standard deviation; Σ sum (total); SFA, saturated fatty acids; UFA, unsaturated fatty acids;

MUFA, monounsaturated fatty acids; *PUFA*, polyunsaturated fatty acids;
UFA/SFA, the ratio between unsaturated fatty acids and saturated fatty acids;
PUFA / MUFA, the ratio between polyunsaturated fatty acids and monounsaturated fatty acids; ***extremely significant ($P < 0.0001$); ^{ns} not significant.

Table 2

The fatty acid compositions (weight %) of tall oils reported in literature

Fatty acids	Fatty acid composition (%)		
	References		
	Yordanov et al., 2008	Keskin et al., 2007	Altıparmak et al., 2007
Palmitic	24	-	-
Stearic	18	2.5	2.1
Oleic	38	50.2	52.7
Vaccenic	-	-	-
Linoleic	20	40.6	38.3
Linolenic	-	6.7	6.9

CONCLUSIONS

The main result of the present work was the determination of fatty acid profiles by GC of two different Romanian crude tall oil samples. The high proportion of saturated and monounsaturated fatty acids in analyzed tall oil is considered optimal from a fuel quality standpoint. In conclusion, the studied Romanian tall oils can be recommended as sources of raw materials for biodiesel, or as sources of additives for petrodiesel.

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