

ASSESSMENT OF SECOND GENERATION BIODIESEL PRODUCTION BY TREATMENT OF FATTY ACID METHYL ESTERS WITH A HYDROGEN RICH GAS

Mihaltan¹⁾ A. I., C. Varaticeanu¹⁾, C. Petcu²⁾, Al. Naghiu³⁾

¹⁾National Institute for Research and Development of Optoelectronics Bucharest – Research Institute for Analytical Instrumentation, Donath 67, 400293 Cluj – Napoca, Romania. e-mail: alin.mihaltan@icia.ro; Fax: +40 264 420667; Tel: +40 264 420590

²⁾Rokura Industrial Applications, Bucharest, Romania. e-mail: cristian.petcu@rokura.ro

³⁾University of Agricultural Science and Veterinary Medicine, Cluj – Napoca, Romania. e-mail: alnaghiu@yahoo.com

Abstract. *The properties of biodiesel depend on the chemical structure of individual fatty acid methyl esters. In this the chemical structure of fatty acid chains was modified by high-pressure, high temperature treatment with a hydrogen rich gas, obtained through the alkaline electrolysis of water, in the presence of Pt as a catalyst. The effect consists in the breaking of the long unsaturated carbon chain of fatty acids methyl esters with the forming of new more volatile compounds, with a shorter and more saturated carbon chain. The hydrogen rich gas presents real applicability in the production of second generation biofuels, but a strict kinetic control and the use of catalyst with high specificity is recommended.*

Keywords: biodiesel, fatty acid methyl esters, hydrogen rich gas, second generation biofuels.

INTRODUCTION

For a sustainable future of the planet, people must look into renewable energy sources which implicitly include sustainable fuel sources. Based on the positive energy balance or life cycle analysis, biodiesel is shown to be sustainable [1]. Despite the invention of vegetable oil fuelled engine by Rudolf Diesel, dated back in the 1900s, full exploration of vegetable oil based fuel such as biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves [2].

There are different technologies of producing 1st generation biodiesel and applications such as direct use and blending, microemulsions, thermal cracking (Pyrolysis) of vegetable oil and transesterification [3-5]. Some methodologies proposed in the past, such as pyrolysis and cracking of oils and fats, can produce compounds that are smaller than their triglyceride source and, therefore, suitable to be used as fuel [5]. However, pyrolysis is not very selective and a wide range of compounds is usually obtained. Fuels obtained by pyrolysis of triglycerides (TG) are less environmentally pleasant than petroleum derived fuels in terms of oxygen content. In addition, solid residues of ash and carbon that are created during TG pyrolysis require additional separation steps. Catalytic cracking has been used in an effort to control the types of products generated by TG cracking, using a vast variety

of catalysts. However, a gasoline-like fuel is more likely to be formed than a diesel-like fuel [6-8].

The most common method of biodiesel production is transesterification (alcoholysis) of oil (triglycerides) with methanol in the presence of a catalyst which produces biodiesel (fatty acid methyl esters, FAME) and glycerol as a by-product. The selection of catalyst depends on the amount of free fatty acid (FFA) present in the oil. Generally, base-catalyzed reaction gives a better conversion in a relatively short time for triglyceride stock with a low content in FFA, while acid-catalyzed esterification followed by transesterification is suitable for higher FFAs containing stock. Because the transesterification reaction is reversible, an excess of alcohol, above the stoichiometric requirements, is used to drive the process forward in order to increase the yields of the alkyl esters and to assist phase separation from the glycerol [9].

Most biodiesel production of today utilizes batch reactors. Biodiesel plants using batch reactors between 500 and 10,000 tons of biodiesel per year [5]. This number can be increased if continuous processing technology is applied. A number of successful experiments resulting in increased biodiesel production from continuous processes have been reported in the literature [10-15].

Although continuous production plants can achieve higher biodiesel throughputs and are less expensive to build and can more easily be adapted to changing raw materials and reaction conditions. This flexibility is particularly important given the economic impetus to use diverse TG feedstock for biodiesel production. Nevertheless, current trend is leaning toward the construction of continuous production plants to ensure sustainability of biodiesel supply [5] and lower operational cost by increasing the volume.

MATERIAL AND METHOD

First generation biodiesel was produced by transesterification of soybean oil, obtained from SC REVIVA SRL (Apahida, Cluj). The physico-chemical characterization of the soybean oil is given in Table 1. The transesterification process was carried out with a 40 % excess of methanol, and in the presence of NaOH. The anhydrous methanol used in the transesterification reaction was purchased from LGC Promochem, and the sodium hydroxide physico-chemical properties were according to STAS 3068.

The catalytic treatment of the fatty acid methyl esters (FAMES) obtained from the transesterification process was carried out in a high-pressure, high-temperature Parr reactor, type 4520 Bench Top Reactor Fixed Head, with a 1000 ml T316 stainless steel reaction vessel, and bench top support stand. Presented in Table 2 and in Figure 1 are the configuration and the side view of the reactor.

The effect of the catalytic treatment of FAMES with hydrogen rich gas (HRG), was comparatively studied in the presence of two catalysts, Pd on a carbon support and a \varnothing 0.08 mm Pt wire, on a 1 % solution of butyric acid methyl ester in n-Hexan (GC, LGC Promochem). Both catalysts were added in the proportion of 1 % in regard to the butyric acid methyl ester.

Table 1

Physic – chemical characteristics of the soybean oil

Parameter	Abbreviation	Chain	Double bonds	Molar mass		U / M	Determined value
Density at 15°C						g / cm ³	0,917
Viscosity at 40°C						cP	27,07
Humidity						%	0,04
Acidity value						mg KOH / g	0,83
Iodine value						g I / 100 g	128,5
Flashing point						°C	301
Palmitic acid	C16	16	0	256	21,53	%	8,41
Stearic acid	C18	18	0	284	9,74	%	3,43
Oleic acid	C18:1	18	1	282	50,51	%	17,91
Linoleic acid	C18:2	18	2	280	166,10	%	59,32
Linolenic acid	C18:3n3	18	3	278	29,38	%	10,57
Arahidic acid	C20	20	0	312	0,87	%	0,28
Behenic acid	C22	22	0	340	1,16	%	0,34
Average molar mass for the soybean oil:					279,29	g / mol	calculus

Table 2

The instrumental configuration of the Parr reactor

Stirring system	16in/lb magnetic stirrer
Safety membrane	PTFE gasket and split ring closure, MAWP 1900 psi at 350 °C
Hatch	Head to include 0 – 200 psi gage, 200 psi set relief valve, 100 psi rupture disc, double valve assby with dip tube, gas release valve and thermowell with thermocouple and serpentine cooling coil
Heating system	Heater assby, 1000 watts
Catalyst support	Static catalyst basket
Input voltage	230 volts
Control system	4857A Reactor Controller, with one control CPU, temperature control module with Thermocouple, Pressure monitoring module with transducer, tachometer, motor current display module operating and configuration software, power controller

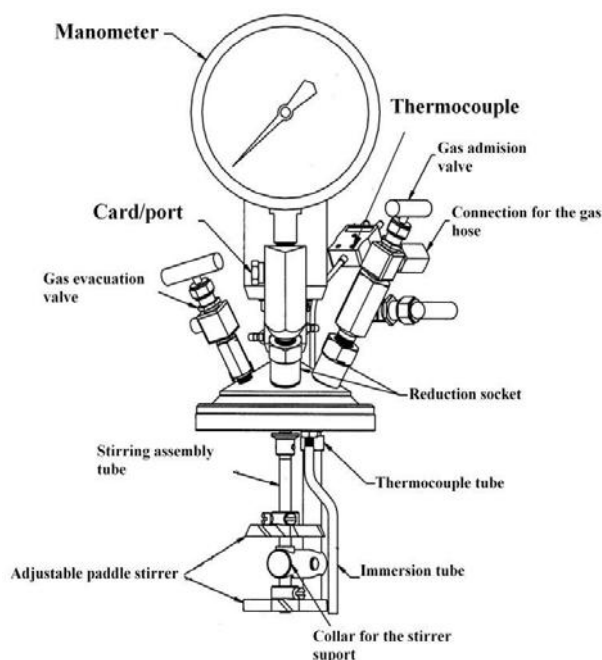


Fig. 1. A side view of the Parr reactor

The treatment of FAMES obtained from the transesterification reaction of soybean oil, with HRG, was conducted on 300 ml of sample, at a temperature of 80 °C and at 5 bars of pressure, under continuous stirring at 1200 rot/min. The sample went through 9 treatment cycles. A cycle consists in 7 periods of 15 minutes each, of reaction time, between the introductions of the HRG gas, and, when the decreasing of the pressure inside the reaction vessel becomes asymptotic, moment in which the reaction rate is very small, the reaction tends to stop. A 2 ml sample was taken after each cycle for gas chromatography analysis.

The soybean oil, the FAMES obtained from the transesterification process, the samples taken from the treatment of the butyric acid methyl ester and the of the FAMES with HRG, were analyzed using an Agilent 7890A gas chromatograph equipped with a flame ionization detector and a DB-WAX capillary column. The instrumental configuration and the operating parameters are presented in Table 3.

Qualitative analysis of the sample taken after the HRG treatment, was carried out with the help of an 6890 Agilent gas chromatograph (Agilent Technologies), equipped with a 30 m x 0.25 mm i.d., 0.25 film thickness, HP-5 MS, (5%-Phenyl)-methylpolysiloxane (Agilent Technologies) fused silica capillary column, connected to an 5975 B Agilent mass spectrometer (Agilent Technologies).

Split less injection was used. The initial oven temperature was set to 50 °C and the temperature was increased to 275 °C, with a temperature increase rate of 10 °C per minute. The injector temperature was 250 °C and the transfer line was held at 220 °C. Mass spectra were recorded after electronic impact (EI) ionization. The mass-to-charge ratio range (m/z) used was 45-400. The ion source temperature was set to 230 °C.

Table 3
The instrumental configuration and the operating parameters of biodiesel analysis using a gas chromatographic method

The instrumental configuration	
Chromatographic system	Agilent 7890
Inlet	Split/Splitless
Detector	FID
Automatic Sampler	Agilent 7683
Column	DB-WAX 30mx0,25mm(d.i), 0,25µm
Operating conditions	
Inlet temperature	250°C
Split ratio	1/50
Injection volume	1µl
Carrier	Helium
Pressure	53kPa
Oven temperature program	50°C, 1min, 25°C/min - 200°C 3°C/min - 230°C, 18 min
Detector temperature	280°C
Detector gases	H ₂ :40ml/min; Air: 450ml/min He make-up: 30ml/min

The HRG generator was provided by Rokura Industrial Applications (Bucharest, Romania). The gas generator works on the principle of alkaline electrolysis of water. This produces a non-stoichiometric compound, known as Hydrogen Rich Gas or HRG made of: H₂, H, O₂, O, H₂O, OH⁻, OH⁺, and H₂O₂, with special physical and chemical properties. The technical data for the HRG generator are presented in Table 4.

Table 4
Technical data for the HRG generator

Input voltage	3 x 380 V
Demineralized water quality	max. 2 µS / cm
Capacity of the HRG reservoir	20 l
Maximum current for electrolysis	20 A
Maximum power consumed at the maximum flow	17 kW
Maximum capacity for HRG production	4.5 Nm ³ / h

RESULTS AND DISCUSSION

According to the quantitative analysis of the products resulted from the treatment of the butyric acid methyl ester with HRG, presented in Figure 2, for the comparative study of the catalytic effect of the two catalysts used, meaning Pd on the carbon support and the Ø 0.08 mm Pt wire, the better results are achieved with the Pt wire, as can be seen from the graph. The peak areas of the resulted compound are bigger for the catalytic treatment in the presence of Pt, than in the presence of Pd.

As a result to this preliminary comparative study, the Ø 0.08 mm Pt wire was chosen as catalyst in the treatment of FAMEs with HRG, with regard to the implementation of a new procedure for second generation biodiesel production

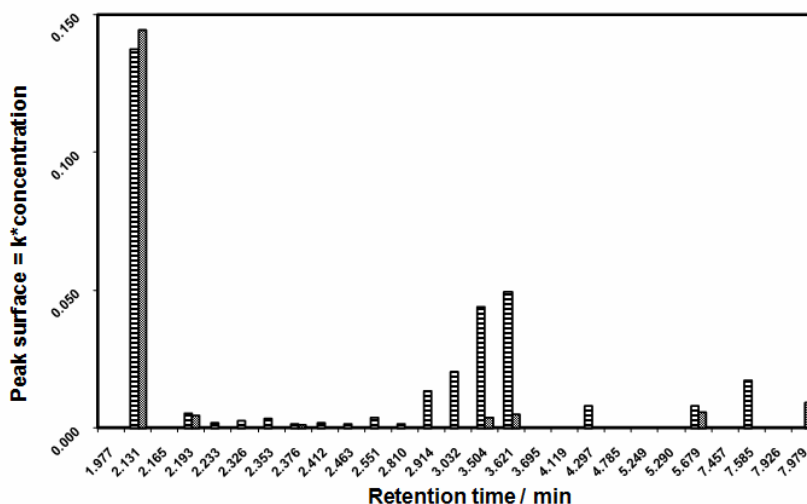


Fig.2. Reaction products of the treatment of butyric acid methyl ester with HRG using as catalysts Pd on carbon support (▨) and Ø 0.08 mm Pt wire (■)

Using the gas chromatography analysis method, the events that took place during the treatment of FAME with HRG, have been studied. The evolution of the composition of the FAME oil is shown in a sequence of three chromatograms, corresponding to the samples taken after the first HRG treatment cycle (figure 3), after the fourth cycle (figure 4), moment corresponding with the middle of the procedure, and respectively at the end of the HRG treatment process (figure 5).

As it is shown in the three following figures, the effect of the high-pressure, high-temperature treatment with HRG is that the long unsaturated carbon chain of the fatty acid methyl esters, was broken and that new, more volatile respectively with a shorter carbon chain compounds, were obtained. It can be observed that the

chromatographic peaks at 10.950; 11.502 and respectively 12.334 minutes retention time, corresponding to the methyl esters of the oleic, linoleic and linolenic acids, which are the main components of FAME oil used as starting material, are completely missing from the chromatogram of the last sample. This fact indicates that these compounds were completely transformed in new compounds, most likely by breaking of their long unsaturated carbon chains in certain points. Most likely the new formed compounds are mono-carboxylic or di-carboxylic acids, alcohols with one or two OH- groups and other species with a carbon chain of six to ten, or even more carbon atoms.

The previous affirmation was confirmed by the GC-MS qualitative analysis of the last sample. The results show that the major components of the newly obtained oil are hexanoic, heptanoic, octanoic, nonanoic, suberic, octandioic and nonandioic acids, respectively some of the methyl esters of the mentioned acids. Because of the complex composition in free radicals of the hydrogen rich gas, particularly H, O, OH⁻, OH⁺, and also of the harsh reaction condition respectively high pressure and temperature and the presence of Pt as a catalyst, it is difficult to predict a reaction mechanism to explain the formation of the new compounds.

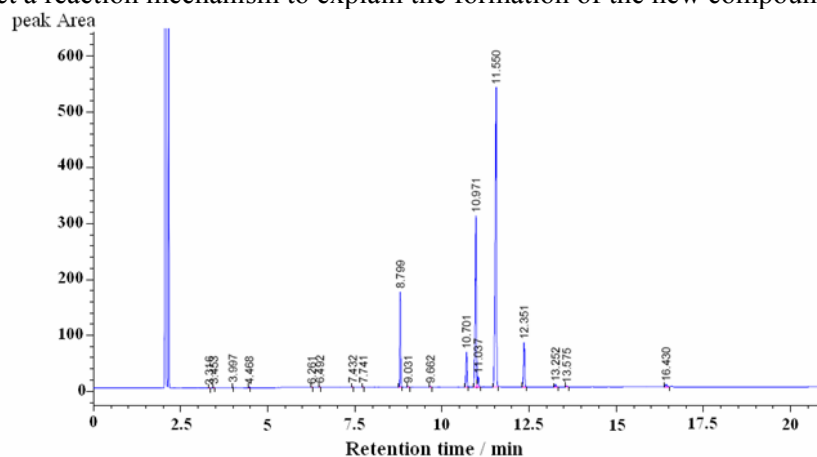


Fig. 3. Chromatogram of the sample taken after the first HRG treatment cycle

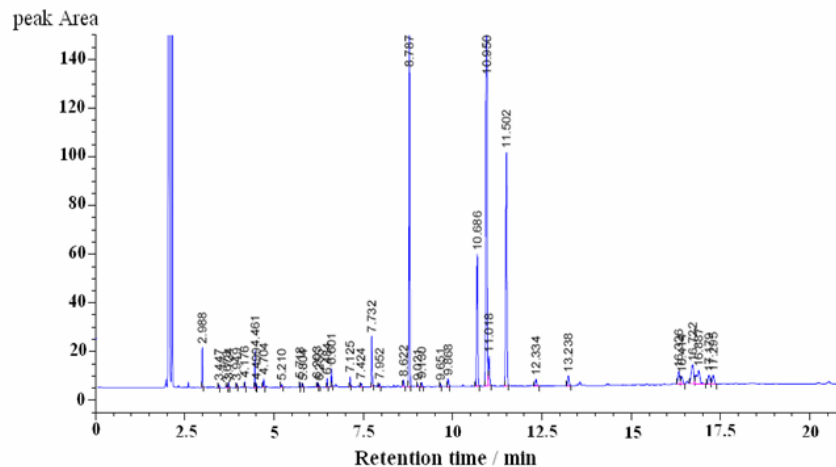


Fig.4. Chromatogram of the sample taken after the fourth HRG treatment cycle

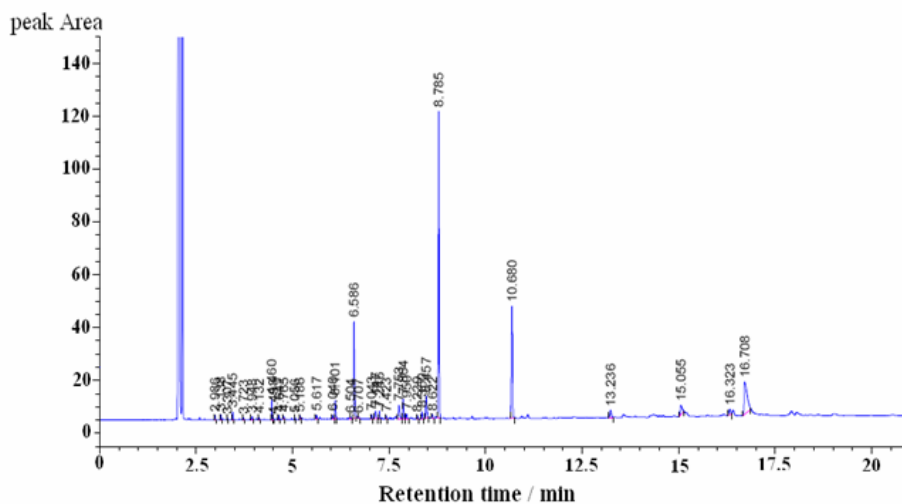


Fig. 5. Chromatogram of the final sample taken at the end of the HRG treatment process.

The overall effect of the HRG treatment of first generation biodiesel, in this case, fatty acid methyl esters, is the increase in the volatility of the newly formed compounds along with the shortening of the carbon chain, facts that makes the new oil closer to gasoline than to biodiesel. This effect can be eliminated by a strict kinetic control of the process and by using catalysts with a higher specificity, for example thermoregulated phase-transfer catalyst for the hydrogenation process [15, 16].

CONCLUSIONS

The effects of the high-pressure, high temperature treatment of first generation biodiesel, particularly FAMES, with hydrogen rich gas produced through the alkaline electrolysis of water, were studied in the presence of Pt as a catalyst. It was shown that the fuel properties of FAMES were altered by the breaking of the long carbon chain of the fatty acids under the harsh reaction condition and the influence of the free radicals from HRG, resulting in shorter carbon chain compounds that possess a higher volatility.

The HRG presents real applicability in the production of biofuels but only with a strict kinetic control of the reaction and using a high specificity catalyst.

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