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Fuel Properties of Biodiesel Produced from Different Raw Materials in Croatia

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During the past decade or even earlier almost all the EU countries, as well as most transition countries, launched the production of biodiesel fuel. Such a trend will continue in the future as it is indicated in the EU Directive (2003/30/EC) on alternative fuels for road transport and measures for promotion of the use of biodiesel. In Croatia, the production of biodiesel started only in 2005. It is based on raw materials which are available in the domestic environment: rapeseed oil and sunflower oil and waste edible oil. Methyl ester produced from rapeseed oil fully meets the EU standard under EN 14214, i.e., quality requirements for biodiesel fuel and may be used as pure (B100) or blended with mineral diesel fuels. Since methyl ester of sunflower oil and waste edible oil in some parameters do not meet the mentioned requirements, it is recommended to use them either as blended with rapeseed methyl ester or blended with mineral diesel fuel, which conforms to the recommendation of the European Union Strategy for biofuels production COM (2006).
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0 INTRODUCTION

Croatia, a country with limited natural resources, is a transitional country in the South-Eastern Europe and a candidate for joining the European Union. Energy consumption in 2004 in Croatia amounted to 412.04 PJ, which is an increase by about 4.1% comparing to 2003. However, in 2005 this value slightly decreased, by 0.1% and was 411.66 PJ. Total energy production in 2005 in Croatia amounted to 197.23 PJ, out of which 20.3% or 40.11 PJ of energy was produced from domestic crude oil sources. However, in the last 10 years we saw a dramatic downfall in domestic crude oil production. For example, in 1990 as much as 104.54 PJ of energy was produced from crude oil, which is approximately 62% more than in 2005. In contrast to this, energy import is constantly increasing, by almost 7.5% annually. The rise in liquid fuel consumption, decline of domestic oil sources and rising price of crude oil on the world market lead, at the end of the last century, to developing programs of more intensified use of renewable energy sources, especially of biodiesel fuel [1].

The energy utilization from biomass resources has received much attention since the mid-1990s. The energy of biomass (also referred to as biomass energy) from plants, animals (fed with plants or other animals) or wastes they produce originally comes from solar energy through the photosynthesis process. The energy supply from domestic waste is especially noted in that it not only enhances fuel diversification, but also eliminates the environmental pollution. Of the many energy productions from food wastes or food processing wastes, waste edible oils seems to be especially attractive based on bioresource sustainability, environmental protection and economic consideration.

The national strategy of the Government of Croatia recommends the adoption of an integrated approach to development covering different sectors: agriculture, energy, environment, tourism, etc. In the frame of this integrated approach and as part of the BIOEN national energy program, the efforts to introduce biodiesel production in Croatia started in 2000. The objective of introducing biodiesel industry is to reduce Croatian energy dependency, comply with the relevant EC Biofuels Directive, help improve the quality of the environment and diversify production and employment in the agriculture and industry sectors. The cultivation of energy/non food crops to produce

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biofuels should be an area of particular interest of the Croatian agricultural policy with the view of creating new economic resources and preserving employment in the rural communities. The production and use of biodiesel to replace fossil fuels in transport also contribute to meeting the signed commitment and targets resulting from the Kyoto Protocol to reduce greenhouse gas emission. Iz should also contribute to enhance the tourism industry by an emphasizing an environment friendly approach [2].

From the utilization perspective, biodiesel and its blends represent an excellent substitute for mineral diesel. Thus, biodiesel features should be benchmarked with mineral diesel features in all their aspects. While consumption features of biodiesel give, generally speaking, rather homogeneous results, its production features vary depending on the source of production. Namely, biodiesel can or could be obtained from various sources such as different vegetable oils, animal fats, recycled edible oil and, even, soapstocks. Consequently, biodiesel production process greatly depends on geographical and climate conditions as well as magnitude and organization of sectors related to use of edible oils, such as catering and households [3]. Here, the focus will be placed on biodiesel originated from the main raw material for biodiesel production in Croatia - rapeseed, sunflower and waste edible oil. They are produced in the first two biodiesel plants in Croatia which started operation in 2006.

Table 1. *Total energy supply during 1995 to 2005 in Croatia*

	PJ						
	1995	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**
Overall energy consumption							
Coal and Coke	7.42	17.15	19.36	22.89	26.18	29.70	32.95
Fuel wood	13.52	15.64	12.24	12.39	15.96	15.88	14.77
Liquid Fuels	146.03	160.52	164.25	175.16	192.85	179.62	181.88
Natural Gas	82.77	94.98	98.87	101.10	100.45	104.66	101.06
Hydro Power	51.75	56.93	65.51	52.01	46.48	69.00	62.40
Electricity	12.59	14.40	11.36	12.68	14.01	13.19	18.41
Renewables	0.0	0.0	0.0	0.0	0.0	0.02	0.20
TOTAL	**314.08**	**359.62**	**371.58**	**376.23**	**395.93**	**412.04**	**411.66**
Primary energy production							
Coal	1.96	0.0	0.0	0.0	0.0	0.0	0.0
Fuel wood	13.52	15.64	12.24	12.39	15.96	15.86	14.77
Crude Oil	62.81	51.35	47.52	47.00	44.61	42.44	40.11
Natural Gas	69.12	59.40	70.86	74.53	76.83	77.08	79.76
Hydro Power	51.75	56.93	65.51	52.01	46.48	69.00	62.40
Renewables	0.0	0.0	0.0	0.0	0.0	0.02	0.2
TOTAL	**199.17**	**183.32**	**196.12**	**185.94**	**183.87**	**204.40**	**197.23**
Energy import							
Coal and Coke	6.76	20.89	18.49	25.13	27.54	33.73	31.51
Crude Oil	176.22	165.57	165.72	180.86	182.41	189.49	182.57
Petroleum products	10.88	9.31	20.11	34.07	31.08	40.01	43.34
Natural Gas	9.31	37.67	36.83	36.87	38.72	35.82	38.56
Electricity	15.77	15.79	13.48	14.14	16.12	19.07	31.49
TOTAL	**218.95**	**249.23**	**254.63**	**291.07**	**295.88**	**318.12**	327.47
Energy export							
Coal and Coke	0.04	0.26	0.10	1.28	1.95	1.28	1.08
Crude Oil	10.48	1.48	0.0	0.0	0.0	0.0	0.0
Petroleum products	90.94	73.01	71.14	68.49	73.06	86.71	79.00
Natural Gas	0.0	0.0	8.0	12.31	11.63	11.82	15.18
Electricity	3.19	1.39	2.12	1.46	2.11	5.88	13.08
TOTAL	**104.65**	**76.15**	**81.71**	**83.54**	**88.75**	**105.69**	**108.34**

Because of the growing crude oil prices, limited resources in fossil fuels and environmental concerns regarding air quality, the objectives of this paper will give a comprehensive review of biodiesel production from main raw materials in Croatia – rape seed oil, sunflower oil and waste edible oil. The main subjects dealt with in this paper are given in the following key elements:

- Current status of total energy supply, and diesel fuel supply and consumption;
- Status of oilseeds and edible oils supply;
- Generation and recycling of waste edible oils;
- Biodiesel production from main vegetable oils in Croatia – rapeseed, sunflower and waste edible oils.

1 CURRENT STATUS OF TOTAL ENERGY SUPPLY, AND DIESEL FUEL SUPPLY AND CONSUMPTION

1.1 Current Status of Total Energy Supply

Croatia is a country rich in renewable energy resources such as biomass, solar energy and wind energy. However, it has limited fossil energy resources such as crude oil and natural gas, which makes Croatia a high energy-importing country

Energy consumption per inhabitant is somewhat below the European average and amounts to 2,215 kgoe per inhabitant. As comparison, Island has the highest energy consumption per inhabitant or 15.638 kgoe, while at the bottom of the list there is Moldavia with only 700 kgoe per inhabitant. The future development of industry and transport sector in Croatia, the energy consumption is expected to rise, so it is necessary to ensure new, either domestic or imported energy sources. In Croatia, industry and transportation sector together use 52.6% of energy, while general sector makes for the remaining 47.4% of energy consume.

In 2005, the total primary energy supply decreases by 3.5% with respect to the previous year. The great fall was recorded in hydro power harnessing because the 2005 was less favorable in hydrological terms than the previous year.

As evident in Table 1, reliance on the imported crude oil of total energy import gradually decreased from 80.48% in 1995, 66.4% in 2000, 61.6% in 2003, and 59.6% in 2004, to 55.8% in 2005. Due to the national energy policy aimed to diversification of the imported energy sources, the second largest imported energy source in 2005 were petroleum products with a 13.2% share in total imported fuels. Other energy supply sources also include natural gas (11.8%), coal (9.6%) and electricity (9.6%) [1].

It is important to note that Croatia also exports a significant amount of energy (Table 1). The highest annual increase of energy export was recorded between 2003 and 2004, by 19.1%. The tendency of growing energy export was maintained and in 2005 it grew by another 2.5%. The most exported products were oil derivatives (73%), natural gas (14%) and electricity (12%).

By 2020, considerable portions of the energy demand will be met by natural gas/liquefied natural gas, hydro power and renewable energy (especially in wind energy and solar energy). This gradual increase in clean and green energy supply is the Croatia’s response to the challenges to be by faced the economic, energy and environmental policies of sustainable development in the near future.

In the future, a gradual reduction in the production of fossil fuels and a rise in energy generation from renewable sources are expected. Renewables should play an increasingly important role in the energy supply. In the period until 2030 the share of fossil fuels will be gradually decreasing so that natural gas and crude oil together will have a share of approximately 25%. The remaining three quarters of primary energy production will consist of energy from renewable energy sources, where hydro power will make for 32%, fuel wood and biomass 19.6%, while other renewables will make for 23.6% (biodiesel included) [1].

1.2 Current Status of Diesel Fuel Supply and Consumption

It is well known that Croatia has its own sources of crude oil. In 2005 Croatia used 4,991,000 tons of crude oil, while its own production was 946,000 tons, which makes up 19% of total crude oil consumption. The remaining 81% of the total demand is met by imported crude oil. It is important to note that crude oil production is constantly falling, which is illustrated by the fact that in 1990 it amounted to nearly 2,496,800 tons.

The data by the Ministry of Economy, Labor and Entrepreneurship on diesel fuel supply and

Table 2. *Diesel fuel production and consumption during 1995 to 2005 in Croatia*

Diesel production and consumption	**10^3 t**						
	1995	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**
Production	1,017.1	1,063.9	1,052.1	1,054.6	1,325.0	1,191.9	1,080.9
Final energy demand	**609.7**	**863.7**	**925.3**	**995.6**	**1,145.7**	**1,221.8**	**1,311.5**
Thermal power plants	4.8	0.0	0.0	0.0	0.0	0.0	0.0
Road transport	360.3	533.2	576.0	658.4	779.9	857.8	927.3
Other transport	80.6	77.8	78.9	81.1	82.9	85.1	85.1
Agriculture	120.1	186.6	202.4	189.5	189.0	183.1	183.0
Construction	43.6	65.4	67.7	76.4	93.9	95.8	110.6

consumption in Croatia are given in Table 2, as well as some important features relevant to diesel fuel supply and demand. The consumption of diesel fuel in Croatia in the last few years has been increasing significantly. Thus as far back as 1995 total consumption of diesel fuel was 609,700 tons, to rise up to 1,331,800 tons in 2005, out of which approximately 78% is consumed in the transportation sector and 14% in agricultural sector [1].

Recently it has been demonstrated that the diesel engines perform much better that gasoline engines in terms of oil saving and greenhouse gases (e.g. carbon dioxide) emission reduction. From the point of view of the global warming concerns and permanent high oil price levels, the diesel fuel consumption is expected to increase in the near future [4].

In the last decade or even earlier almost all the EU countries as well as most transition countries have started the production of biofuel: biodiesel and ethanol. Such a trend will continue in the future as it is shown in the EU Directive (2003/30/EC) concerning alternative fuels in road transport and measures for biofuel promotion. This document proposes the following measures, which, when accepted, will become an obligation for the EU candidate countries, which includes Croatia as well: by 2010 an amount of 5.75% of conventional fuels used for transport should be replaced by alternative ones; EU Member States have the right to apply differentiated tax rate on biofuels in order to encourage their use; by 2007 the share of biofuels in the European Union should amount to at least 3.5% [5].

It should be emphasized that these Directives are mandatory, which means that the projected fuel switch must be accomplished. These directives have been accepted by all EU Member States, but they must also be accepted by the future European Union members. This means that these obligations must be taken on by the Republic of Croatia as one of the future EU Member States.

2 STATUS OF OILSEEDS AND EDIBLE OILS SUPPLY FOR BIODIESEL PRODUCTION IN CROATIA

2.1 Status of Oilseeds Supply

The most significant plants for vegetable oil production in Croatia are sunflower, soy, and rapeseed [6]. Which raw material will be chosen for biodiesel production depends only on specific conditions of a country concerned (climate, populations' consumption patterns, standard agricultural plant production, etc). However, the most important raw materials for production of biodiesel fuel are rapeseed and sunflower. Unlike these, soy has higher protein content (ca 40%), and lower oil content (ca 20%), which makes it a very convenient source of animal feed. In addition, oilseed crop represent necessary cultures in the crops rotation plan and enable the optimum production of other crops [7].

The production of oilseed crops in Croatia is exercised at approximately 90,000 hectares and is focused on 3 plants: soybean, sunflower and rapeseed, with soybean dominating in acreage and yield. Table 3 shows the production and yield of the main oilseed crops as potential sources of biodiesel fuel in Croatia – rapeseed and sunflower [8].

Table 3. *Production and yield of rapeseed and sunflower in Croatia in the period 1995 to 2003*

Year	Production (t)		Area (ha)		Yield (t/ha)	
	Rapeseed	Sunflower	Rapeseed	Sunflower	Rapeseed	Sunflower
1995	24,472	10,982	19,385	37,066	2.23	1.91
2000	29,436	53,956	12,886	25,715	2.28	2.10
2001	22,456	42,985	10,319	25,336	2.18	1.70
2002	25,585	62,965	13,041	26,835	1.96	2.35
2003	28,596	69,253	15,530	28,165	1.84	2.45

It is clear that oilseed crops production in the Republic of Croatia is relatively low and that it varies significantly. It is interesting to note that the share of oilseed plant production in total arable crop production decreased. The factor that causes most concern is exceptionally low yield, ranging from 1.70 t/ha to 2.45 t/ha for rapeseed and 1.84 t/ha to 2.28 t/ha for sunflower (actual yield depending on the year of production). This emphasizes the importance of plant production technology in oilseed crop production. Low yields in rapeseed production are not surprising if we take into consideration that this crop is most often grown on poor and ill-cultivated soils where water supply and air properties are inadequate and sizeable depressions create water pools which lead to plant spacing reduction. Other reasons that rapeseed is grown on small areas and that crop yields and production give average result lie in obsolete and inadequate machinery, insufficient application of updated know-how, poor crop protection measures and modest skills and knowledge of family farm owners. Low interest of producers and low share of rapeseed in the crops mix on our fields are the result of the economic policy in the agricultural sector, in particular price policy, and from low interest shown by the processing industry.

Further expansion of the areas under the rapeseed, as a primary raw material for biodiesel fuel is possible only if such areas are significantly increased in the current narrow crop rotation plan and by re-cultivation of deserted and undeveloped land. This would provide new areas in a properly planned crop rotation. This is a realistic option for increasing rapeseed production and rising average yields up to 3.0 to 3.5 tons per hectare, which is feasible both in agro ecological and technological terms. In this way the production of rapeseed in the newly sown areas would increase by over 30% and ensure the raw material for biodiesel production.

2.2 Starting Materials for Biodiesel Production in Croatia

2.2.1 Rapeseed Oil

Rapeseed oil (*Brassica napus L. ssp oleifera*) was originally chosen for transesterification experiments by biodiesel pioneers because of its low price compared to other readily available vegetable oils. However, it soon became apparent that thanks to its high content of monounsaturated oleic acid and the low levels of both saturated and polyunsaturated acids, this oil is practically an ideal raw material by its combustion characteristics, oxidative stability and cold temperature behavior. Due to its favorable properties, rapeseed oil is still the feedstock of choice in most European countries, including the world's largest biofuel producers, Germany and France [9].

Rape seed contains 40 to 48% oil and 18 to 25% proteins. The rapeseed oil belongs to the group of semi-drying oils with iodine number 95 to 120, and is used for human nutrition (as refined oil) and for technical purposes (biodiesel fuel, detersive and soap production, etc). Intensive and efficient breeding activity created new rapeseed cultivars ("00"), improved quality of oil and crushed oilseed. In triglycerides of these cultivars, dominant is oleic acid (over 60%) instead of erucic acid. The linolenic acid content is reduced (below 10%), and the linoleic acid content is raised to 18 to 20%. This change in fatty acid content improved the consume value of rapeseed oil and it can match the best quality oils. Today, canola oil ("00" Canadian cultivars' oils) contains erucic acid only in traces, 5 to 8% saturated oils, 60 to 65% monosaturated oils and 30 to 35% polysaturated fats. Table 4 shows the normal content of fatty acids of rapeseed, with and without erucic acid. [7].

2.2.2 Sunflower Seed Oil

Sunflower (*Heliantus annuus. l. p.*) is an arable crop grown for its seed. In addition to oil and protein, the sunflower seed contains several important minerals and other substances. Hybrids grown at present contain mostly between 45 to 53% oil. The oil contains mainly fatty acids (80 to 90%) as well as linoleic (up to 60%) and oleic acid.

Helianthus species comprises many varieties, two of which are important for the production: common sunflower and Jerusalem Artichoke. Hybrids have been used in the Republic of Croatia since 1975. Vegetation period lasts from 2.5 to 5 months [10].

Sunflower seed oil (*Helianthus annuus*) comes second in the list of vegetable oil sources for biodiesel production in Europe. Undoubtedly recognized as a valuable oil source for human nutrition, its high content of linoleic acid puts limit to the use of sunflower seed oil for fuel production. According to the European biodiesel standard (EN 14214) pure sunflower oil methyl esters cannot be used as a fuel for diesel engines, as it exceeds the limit for iodine value set at ≤ 120 g I_2/100g. Moreover unadditivated sunflower oil fuels will also give poor ratings for oxidative stability. To solve this problem, cultivars enriched in oleic acid have been developed [9].

Table 4 shows the fatty acids content in sunflower. Unlike rapeseed oil with dominant oleic acid, sunflower mostly contains linoleic acid (71.5%), followed by oleic acid (15.9%).

2.3 Generation and Recycling of Waste Edible Oil

Waste edible oil is a very popular raw material for biodiesel fuel production, due to the fact that its treatment is both cost efficient and ecologically beneficial. Because of the fact that the refined waste edible oil has been sold at half price of crude rapeseed oil since as early as 1999, the use of this type of material in biodiesel fuel production contributed to it economic value, which lead to multiple growth in this type of production [9]. Today in Austria the waste edible oil is equal to rape seed oil as a raw material for production of biodiesel fuel. Biodiesel fuel produced from such oil was out at the market in 1992 and since 1994 it has been used as official fuel in the public transport in Graz. At the end 2005 city of Graz had over one hundred buses which use this type of fuel, making total mileage of over 6 million kilometers. So far no difficulties have been noted in using biodiesel fuel produced from waste edible oil.

Table 4 shows the fatty acid content in waste edible oil. It is evident that waste edible oils, in addition to higher oleic acid content (43 to 52%), have higher palmitic acid content as well (13 to 25%). Given the mentioned values, it can be assumed that in waste edible oils prevails palmitic

Table 4. *Normal fatty acids content in rapeseed oil (with high and low erucic acid content), in sunflower oil and waste edible oil*

Fatty acid	Fatty acid content (% in oil)			
	Rapeseed		Sunflower	Waste edible oil
	Withoout erucic acid	With erucic acid		
Palmitinic acid (C 16:0)	3.5	2.2	5.9	13 to 25
Stearinic acid (C 18:0)	1.5	1.5	5.2	5 to 12
Oleic acid (C 18:1)	60.2	11.2	15.9	43 to 52
Linolic acid (C 18:2)	21.3	13.6	71.5	7 to 22
Linolenic acid (C 18:3)	10.9	7.7	traces	0.5 to 3
Eicosenoic acid (C 20:1)	1.3	6.1	-	1.0
Erucic (C 22:1)	0.5	55.1	-	0.5
Nervonic acid (C 24:1)	traces	2.5	-	-

oil which is mostly used in catering industry for multiple uses in deep fryers [11].

The use of vegetable oils for frying results in substantial amounts of waste oils, which then cause the disposal problems. Therefore, the principle reason for using waste oils as raw material for biodiesel fuel production, in addition to lower price, is lies in fact that it solves the problem of its disposal. Acid catalyst processes in biodiesel fuel production from waste edible oil are competitive in economic terms to alkaline catalyst processes applied on crude vegetable oils. Waste edible oils in principle contain some decomposition products of vegetable oils and other substances. A potential problem in biodiesel fuel production from waste oil may arise from its poor physical and chemical performance in the low-temperature conditions due to higher level of saturated fatty acids. At present this is solved by applying additives and adjusting it for use during winter months [11].

Physical traits of methyl ester obtained from waste dibble oil slightly differ from those of methyl esters obtained from crude vegetable oils. The differences are noted at low temperatures, where methyl esters have weaker properties than methyl esters of crude vegetable oils. Due to this, in winter conditions biodiesel fuel from waste edible oil must be blended with mineral diesel fuel.

Biodiesel fuel production from waste edible oil is identical to that which uses animal fats raw material. However, the waste edible oil analysis determined very slight differences between used and unused oils, which can be solved by heating up and filtration of solid particles which are redundant for the foregoing transesterifications.

Although the fuels from edible oils cannot fully replace mineral diesel fuel, they play an important role as alternative fuel which may contribute to the main objective – energy self-reliance and security [9].

2.4 Biodiesel Production from Main Vegetables Oil in Croatia as a Raw Material – Rape Seed, Sunflower and Waste Edible Oils

Biodiesel and its blends represent an excellent substitute for mineral diesel which offers a variety of benefits, increased employment, development of rural areas, increased security of energy supply and a better overall trade balance. However, biodiesel is still not cost competitive with mineral diesel without subsidies or tax incentives except in cases where oil prices are extremely high and vegetable oil prices low [11].

Feedstock cost is the main factor affecting the competitiveness and profitability of biodiesel production, aside from its final cost on the market, and as such it is highly important to clearly identify and quantify current and potential feedstock (in terms of both availability and price), as well as to summarize factors that may impact the identified feedstock use for biodiesel fuel. To increase national rapeseed production, some measures from the Croatian government are necessary in the agricultural sector in order to encourage the rapeseed production. These measures would have to ensure, at least, the quantities of feedstock required for the planned production of biodiesel, increase the yield of rapeseed per hectare and regulate market channels for produced rapeseed and include financial incentives and continuous training and expert support for farmers as the most important components [2].

Many researchers have concluded that due to their low volatility and high cetane number vegetable oils and their derivatives carry more potential as alternative fuels for diesel engines rather than spark-ignited engines. However, the use of crude vegetable oils for diesel engines can cause numerous engine-related problems. The increased viscosity and low volatility of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking [12]. However, these effects can be reduced or eliminated through transesterification of the vegetable oil to form an alkyl ester [13]. The transesterification process removes glycerin from the triglycerides and replaces it with the alcohol used for the conversion process [14]. This process decreases the viscosity but maintains the cetane number and the heating value.

The energy obtained from waste edible oils is a form of renewable energy and, in principle, utilizing this energy does not add carbon dioxide, one of the major greenhouse gases, to the atmospheric environment, in contrast to fossil fuels [15]. Due to the extremely low contents of sulphur and nitrogen in the food waste, its direct utilization as fuel in the combustion utilities (e.g. internal combustion engine) generally generates less environmental pollution and health risks as compared to traditional fossil fuels.

By way of transesterification, the reaction of triglycerides with alcohol (e.g. methanol) under the caustic catalyst (e.g. potassium hydroxide) is processed to produce glycerol and monoalkyl esters, which are known as biodiesel and can be potentially used as alternative diesel fuels in compression-ignition (diesel) engines [16]. Biodiesel, as one of green fuels and/or clean energies, is compatible with traditional petroleum-based diesel and they both can be completely blended without any stratification. From the viewpoint of their chemical composition and properties, biodiesel fuels are biodegradable, low toxic, and release less air pollutants than hydrocarbon-based diesel. However, the use of biodiesel will be faced with the problem of high costs, when compared to petroleum-based oils, and some problems related to the decreased power output and torque force and to the increase in NOx emissions with increasing biodiesel content in the blends [17].

The catalytic conversion of waste edible oil by the transesterification process into biodiesel fuel has the advantage of both economic and environmental benefits. In this regard, the biodiesel fuel proved to be successfully produced from waste edible oils by an alkali-catalyzed transesterification process, and can be considered as alternative fuels for diesel engines and other utilities [18].

Table 5 shows the properties of biodiesel fuel produced in the lab-scale plant installed at the Faculty of Agriculture of the University of Zagreb, using three major raw materials available from domestic sources: rapeseed oil, sunflower oil, and waste edible oil. The analyses were carried out in the independent national laboratories for diesel fuel research in Croatia and Slovakia, and at the Faculty of Agriculture of the University of Zagreb. The methods applied in the analyses are also given in Table 5.

Biodiesel fuels generally display higher densities than mineral diesel, which is also reflected by the respective limits within the FAME standard (860 to 900 kg/m^3 at 15°C) and the EU fossil diesel norm EN 590 (820 to 845 kg/m^3 at 15°C). This difference has impacts on heating value and fuel consumption. Table 5 shows that investigated methyl esters remain within the limits laid down

Table 5. *Properties of biodiesel fuel produced from the lab-scale biodiesel plant*

Property		Unit	Rape seed ME	Sunflower ME	Waste edible oil ME	EN 14214	Tested method
Density at 15°C		kg/m^3	876.90	874.80	876.50	860 to 900	EN ISO 3675
Refraction index at 20°C		-	1.45722	1.45630	1.45581	≥1.490	ASTM D 1298
Sulphur content		mg/kg	≤10	≤10	≤10	≤10	EN ISO 20846
Kinematic viscosity at 40°C		mm^2/s	5.83	5.05	5.99	3.5 to 5.0	EN ISO 3104
Cloud point		°C	-1	0	-1	-	EN 23015
Pour point		°C	-7	-2	-5	-	ASTM D 97
CFFP		°C	-10	-2	-2	<0 (summer) <-15 (winter)	EN 116
Flash point		°C	157	149	126	≥120	EN ISO 3679
Calorific value		MJ/kg	38.3	38.2	37.5	≥35	DIN 51900-3
Cetane number		-	52	48	52	≥51.0	EN ISO 5165
Destillation	beginning	°C	181.6	181.7	179.5	-	-
	10%	°C	209.3	209.4	208.9	-	-
	20%	°C	224.1	224.1	224.0	-	-
	50%	°C	263.8	263.7	264.1	-	-
	90%	°C	334.1	333.9	337.9	-	-
	end	°C	375.3	375.1	378.5	≤385	-
Free fatty acid content		%	0.173	0.188	0.152	<3	AOAC (1999)
Acid value		mg KOH/g	0.346	0.376	0.304	≤0.5	pr EN 14104
Saponification number		mg KOH/g	184.70	183.40	189.90	185 to 190	AOAC (1999)
Iodine value		g I_2/100 g	111.00	128.40	98.30	<120	pr EN 14111

in EN 14214 and that the differences between them are not relevant.

The refractive index (or refraction index) of a medium is the inverse ratio of the phase velocity of a wave phenomenon such as light or sound and the phase velocity in a reference medium. Refraction index of biodiesel should be minimum ≥ 1.490 and from the Table 5 it is obvious that the investigated samples did not meet the requirements.

Fuels with high sulphur content have been associated with negative impacts on human health and on the environment, which is the reason for the current tightening of national limits. Sulphur is limited to a maximum content of 10 mg/kg in the European biodiesel standard. The analyzed methyl esters meet this requirement and they can be added to mineral diesel fuel as "sulphur free" additive.

Fuel viscosity is regulated by the standards at 40°C (Table 5). Viscosity temperature dependence is a very important characteristic of each fuel, because transportation means operate in a wide range of climatic conditions. The viscosity of vegetable oils is significantly higher than that of mineral diesel fuel and it is the main reason why they are not directly applied in diesel engines as fuel and the aim of transesterification is to lower the viscosity of vegetable oils. Kinematic viscosity of biodiesel at 40°C is 3.5 to 5.0 mm^2/s and it is twice as high as diesel fuel viscosity 2.4 to 2.6 mm^2/s. Viscosity, which is a measure of flow resistance of a liquid due to internal friction of one part of a fluid moving over another, affects the atomization of fuel upon injection into the combustion chamber and thereby, ultimately, the formation of engine deposits. The higher the viscosity, the greater the tendency of the fuel to cause such problems [14] Determination of kinematics viscosity values of selected vegetable oils and their respective methyl esters shows that there all fall within the same viscosity range. However, these values are somewhat above those laid down in EN 14214.

De Filippis et al [19] showed that the viscosity of a fuel sample might serve as an indication of its methyl ester content. Their study was based on the fact that the viscosities of other possible biodiesel components, such as free fatty acids, mono-, di-, triglycerides and glycerol, are higher than those of the methyl esters due to higher molecular weights or stronger intermolecular forces. Thus, after calibration with samples for which the methyl ester contents have been determined via capillary gas chromatography, a single determination of viscosity allows the estimation of the methyl ester content within 3% error.

The behavior of fuels under low environment temperature is an important quality measure. Partial solidification in cold weather may cause blockages of fuel lines and filters, leading to fuel starvation and problems during the engine start-up. In order to assess biodiesel fuel performance in cold-temperature various parameters have been suggested, including cloud point (CP), pour point (PP) and cold-filter plugging point (CFPP). Cloud point, denoting the temperature at which first visible crystals are formed within a fuel sample when it cooled, whereas pour point, standing for the lowest temperature to which the sample may be cooled while still retaining its fluidity. Neither of these parameters is considered as a reliable tool for predicting actual engine operability limits and they are not included in biodiesel norm [20] and [21].

Flash point is a measure of the flammability of fuels and thus an important parameter of assessing hazards during fuel transport and storage. As reflected by the limit within the respective standards (≥ 120°C for FAME as opposed to >55°C for mineral diesel), flash points of diesel samples are only about half the values of those for biodiesel. The highest flash point was determined in methyl ester obtained from rapeseed oil (157°C), whereas the lowest one was found in methyl ester obtained from waste edible oil (126°C).

Calorific value is the quantity of heat energy, discharged by fuel at the time of combustion under the set conditions of the experiment. Lower calorific value is applied to internal combustion engines which evaluate the heat losses for water vaporization which occurs because of the oxidation of hydrogen of the fuel. This heat can be discharged only at the time of condensation of vapors in exhaust gases following the limits of a diesel engine. Calorific value is directly related to elemental composition of fuel [22]. This parameter is not included in diesel fuel standard, but it is a limited parameter within the standard for methyl esters used as heating fuels (EN 14214), requiring a minimum of 35 MJ/kg for heating value [9]. It is evident that all investigated methyl esters meet the mentioned requirement so, in addition to their normal use as a fuel they can also be used for thermal energy generation.

Cetane number is a characteristics of fuel which shows the ability of self ignition in the cylinder of a diesel engine. It is determined through experiments in a standard single-cylinder engine. Cetane number depends on fuel composition and influences the start of a diesel, the beginning of the combustion process, equal operation of a diesel and the emission of exhaust gases. Cetane number of biodiesel is higher than that of diesel fuel [22]. Generally, the cetane number is a dimensionless descriptor of the ignition quality for diesel fuel. Both EN 14214 and EN 590 standards require a minimum cetane number of 51. As shown in Table 5, all investigated methyl esters display higher cetane number than fossil diesel, which is considered to be a significant advantage in terms of engine performance and emission [23]. However, a significantly lower cetane number value was determined in methyl ester of sunflower oil, which is below required standard under the norm EN 14214.

Limits for the respective proportions of condensates recovered by atmospheric distillation of fuel samples at specified temperatures are included in the European fossil diesel standard. It is evident from Table 5 that in investigated samples the determined value is within the range set out by te norm EN 14214. These values give hints at the presence of extremely high-boiling compounds, which are associated with the formation of engine deposits, or low-boiling substances, which negatively affect flash point. Whereas distillation characteristics are considered as important quality parameters in fossil diesel fuels, they are only minor relevance in biodiesel. Most biodiesel fuels mainly consist of methyl esters of C_{16} and C_{18} fatty acids, which have almost identical boiling points, whereas fossil diesel are complex mixtures of aliphatic and aromatic hydrocarbons whose boiling points widely diverge [9].

The free fatty acid is a key parameter for determining the viability of the vegetable oil transesterification process [24]. In order to carry out the base catalyzed reaction to completion, a free fatty acid (FFA) value lower than 3% is needed, which was at the same time established in all investigated samples. The higher the acidity of the oil, the smaller is the conversion efficiency. The excessive, as well as insufficient amount of catalyst may cause soap formation.

Acid value or neutralization number is a measure of mineral acid and free fatty acids contained in fuel sample. This parameter also mirrors the degree of fuel aging during storage, as it gradually increases due to hydrolytic cleavage of ester bonds. The obtained methyl esters fully meet the requirements of the norm EN 14214 of ≤ 0.5 mg KOH/g.

Saponification value is the number of milligrams of potassium hydroxide or sodium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. Saponification itself is the hydrolysis of an ester under basic conditions to form an alcohol and the salt of a carboxylic acid. Saponification value should be within the range of 185 to 190 mg KOH/g, which was found only in the methyl ester of waste edible oil.

Iodine value is a measure of total instauration within a mixture of fatty materials, regardless of the relative shares of mono-, di-, tri- and polyunsaturated compounds. The high iodine value shows the unsaturation of fuel which leads to the formation of sediments and can cause the problem of stability of fuel [22]. Under the European biodiesel norm it is limited to ≤ 120 g I_2/100 g. Moreover, EN 14214 also sets out the maximum content of linolenic acid methyl ester and polyunsaturated fatty acid methyl ester to 12% and 1% (m/m), respectively. Engine manufactures have long argued that, when heated, fuels with high iodine value tend to polymerize and form deposits on injector nozzles, piston rings and piston rings grooves [9]. The limit of 120 g I_2/100 g required by the European biodiesel norm excludes several potential oil sources – such as sunflower seed oil, unless the resulting ester are blended with suitable biodiesel types or fossil diesel fuel.

In addition to the standardized procedure for the determination of fatty acid methyl ester contents in biodiesel fuel, several other methods have also been suggested, mainly serving as simple and fast means of process control. Samples directly drawn from the transesterification reaction mixture can be subjected to thin-layer chromatography, which allows a rough assessment of the degree of conversion and therefore facilitates the optimization of reaction parameters.

Table 6. *Composition of fatty acids in methyl esters obtained from rapeseed oil, sunflower oil and waste edible oil*

Measured value	Unit	Rape seed ME	Sunflower ME	Waste edible oil ME	Required value
C 18:1 trans	%	0.70	0.00	3.80	-
C 18:2 trans	%	0.10	0.00	1.20	-
C 18:3 trans	%	1.10	1.20	0.90	-
Total trans isomers	%	1.90	0.00	5.90	-
C 12:0 Lauric acid	%	0.00	0.00	0.20	-
C 14:0 Myristic acid	%	0.10	0.00	0.30	-
C 16:0 Palmitic acid	%	5.00	4.20	11.40	3.3 to 6.0
C 16:1 Palmitoleic acid	%	0.00	0.00	0.40	0.1 to 0.6
C 17:0 Heptadecanoic acid	%	0.00	0.00	0.10	-
C 17:1 Heptadecenoic acid	%	0.00	0.00	0.10	-
C 18:0 Stearic acid	%	1.60	1.50	4.40	1.1 to 2.5
C 18:1 Oleic acid	%	63.40	65.60	52.40	52.0 to 66.9
C 18:2 Linoleic acid	%	19.70	18.70	26.20	16.1 to 24.8
C 18:3 Linolenic acid	%	8.30	8.40	2.70	6.4 to 14.1
C 20:0 Arachidic acid	%	0.40	0.40	0.40	0.2 to 0.8
C 20:1 Eicosenoic acid	%	1.10	1.00	0.70	0.1 to 3.4
C 20:2 Eicosedienoic acid	%	0.00	0.00	0.00	0.0 to 0.1
C 22:0 Behenic acid	%	0.20	0.20	0.40	0.0 to 0.5
C 22:1 Erucic acid	%	0.00	0.00	0.10	0.0 to 2.0
C 22:2 Docosadienoic acid	%	0.10	0.00	0.10	-
C 24:0 Lignoceric acid	%	0.00	0.00	0.00	0.0 to 0.2
C 24:1 Nervonic acid	%	0.00	0.00	0.00	0.0 to 0.04

It is evident from Table 6 that the composition of methyl esters of rapeseed and sunflower oil is within the limits found in references sources [11]. It shows that in investigated methyl esters oleic fatty acid is dominant, followed by linoleic acid. In methyl ester obtained from waste edible oil the concentration of palmitolec, stearic and linoleic acids are above set out levels, while the concentration of linolenic acid is below the required levels. It can be established that the composition of fatty acids of waste edible oil demonstrated poorer qualities than methyl ester obtained from rapeseed and sunflower oil.

3 CONCLUSION

In the past decade, the relation between energy consumption and environmental pollution as well as diversification of energy supply have been in the focus of environmental protection and economic activities aimed at achieving sustainable development and creating renewable energy in the Republic of Croatia. Because of the limited oil reserves and growing environmental concerns, alternative fuels from agricultural resources will become increasingly important in the near future.

Moreover, it can be concluded that the Republic of Croatia has the capacities for production of oil crops as the most important raw materials for the production of biodiesel fuel. Since the Republic of Croatia today has approximately 300,000 hectares of uncultivated land, the production of oil crops for biodiesel fuel is more than necessary. From the viewpoint of resource recycling and use of energy, biodiesel fuel from waste edible oil for diesel engines can be considered as one of green energies.

In case that methyl ester is used for blending with mineral diesel fuel it can be used regardless of whether it is produced from rapeseed, sunflower or waste edible oil. Blending up to 5 % of methyl ester obtained in this way (in conformity to the European quality standard for mineral diesel fuel EN 590) positive effects are achieved in terms of quality of exhaust gases and mineral diesel fuel combustion in the engine.

However, if biodiesel fuel is used in its pure form (B100), it is allowed to use methyl ester produced from rapeseed oil, which is, unlike methyl ester from sunflower oil and waste edible oil, fully conform to the European standard for biodiesel fuel quality EN 14214. Methyl ester of sunflower and waste edible oil can be used in its neat form (B100) with added methyl ester from rapeseed oil which improves its combustion properties in conformity to the mentioned standard. The same recommendation is given by the EU Strategy for biofuels production COM (2006) [25]. It recommends blending the rapeseed oil methyl ester with methyl esters of lower quality.

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