

NEW TECHNOLOGIES IN THE PRODUCTION OF MOTOR FUELS FROM RENEWABLE MATERIALS

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This work presents resources of the Autonomous Province of Vojvodina available for bioethanol and motor fuels (gasoline and diesel fuel) from sustainable resources: corn-stalks, straw, sweet sorghum, pork fat.

The physicochemical basis for novel processes for motor fuel production is coupling microwave pyrolysis of oil shale and catalytic cracking of purified pyrolysis oil, hydrothermal liquefaction of algae and swine manure.

The effects of the degree of purification of crude pyrolysis oil and oil shale on the degree of their conversion to gasoline and diesel fuel, as well as the product distribution are investigated.

*The effects of the duration and temperature of hydrothermal liquefaction of micro-alga, *Botryococcus braunii*, and swine manure on their degrees of conversion into biooil and its thermal properties are investigated.*

The development of novel strategy of biofuel in the Autonomous Province of Vojvodina is presented.

Key words: *biomass, biofuel, oil shale, algae, hydrothermal liquefaction*

Introduction

Biofuels are solid, liquid or gaseous materials which contain sustainable biomass or which can be obtained from it.

The world economic crisis in the 70s of the last century resulted in the increase of crude oil price by 8 times during few months and revealed the truth about limited resources of crude oil in the world. Also, it initiated and strengthened researches devoted to discovering alternative biosustainable raw materials and novel technologies for motor fuel production by using biosustainable raw materials.

The first generation of liquid biofuels: bioethanol (produced from corn grain) and biodiesel (produced from soybean oil or oil-seed rape) was produced, and has been produced ever since from biomass which is mainly used for food for people and animals and for that reason has been strongly criticized [1].

The raw materials for a so called second generation biofuel production are various lignocelluloses materials, such as cornstalks, straw, sugar beet bagasse [2].

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The third and the fourth generation of biofuels which is predicted to become the dominant type of motor fuel will be produced from so called non-traditional highly productive raw materials: algae, bacteria, yeasts and CO₂ [3].

The Autonomous Province of Vojvodina (APV) has strong potential for all above mentioned generations of biofuel.

The tab. 1 presents estimated annual demand of gasoline, diesel fuel, bioethanol, biodiesel of the Republic Serbia in 2015 and current potential of APV for biodiesel production from various lignocelluloses waste materials and pork-fat.

Table 1. Estimated annual demand of gasoline, diesel fuel, bioethanol, biodiesel of the Republic of Serbia in 2015 and current potential of AP Vojvodina for biodiesel production from various lignocelluloses waste materials and pork fat

Materials	Motor fuel [10 ⁶ t per year]				
	Bioethanol	Biogasoline	Gasoline	Diesel	Biodiesel
Cornstalk	1.40	0.82			0.72
Straw	2.1	1.26			1.11
Sweet sorghum	3.15	1.89			1.67
Sugar beet bagasse	0.11	0.06			
Pork fat					0.20
Annual demand	0.23		1.5	2.5	0.37

Based on the results presented in the tab. 1, it is easy to conclude that APV can provide required amounts of biomass which are sufficient to cover the demand of the APV and Serbia for motor fuel.

This paper presents main physicochemical and technological basis for novel processes for motor fuel production from so called nontraditional materials: pyrolysis of oil from oil shale, algae and swine manure.

Motor gasoline production by catalytic cracking of pyrolysis oil from oil shale

Oil shale is a sediment rock with variable content of organic materials (kerogen) from which oil (synthetic crude oil) is obtained by pyrolysis.

The generic type of oil shale is determined by the quantity and structure of kerogen and serves as basic parameter for determining the quality of oil shale and for estimating the possibility for its processing.

It is found out that in Serbia there are 23 pools of oil shale with estimated inner resources from 4.7·10⁹ tons from which it is possible to produce as much as 380·10⁶ tons of pyrolysis oil [4].

By applying conventional procedure for oil shale pyrolysis at 500 °C, crude pyrolysis oil, gaseous fraction, polycoke and ash are obtained from oil shale. Crude pyrolysis oil is then treated by hydrogen producing a so called synthetic crude oil.

Adnadjevic [5] has investigated the effects of catalytic cracking temperature on the degree of conversion of pyrolysis oil obtained by microwave pyrolysis of oak tree sawdust. Bearing that in mind, this paper has investigated the effects of the degree of purification of crude pyrolysis oil obtained from oil shale on the degree of its conversion during the catalytic cracking into the gasoline and diesel fraction.

Materials and methods

Raw materials: pyrolysis oil from Aleksinac oil shale obtained by fast microwave pyrolysis. The content of ash, sulphur and nitrogen compounds and Conradson coke are determined by standard procedures [6]. Catalyst for hydrodesulphurization and denitrogenation is synthesized by the procedure of Kittrell [7].

Physicochemical properties of the catalyst for hydrodesulphurization and denitrogenation are given in tab. 2.

Catalytic hydrodesulphurization and denitrogenation of pyrolysis oil is performed in stainless steel reactor with fixed layer of catalyst under the following conditions: $T = 400\text{ }^{\circ}\text{C}$, $p = 100\text{ atm}$; space velocity of pyrolysis oil: $\alpha = 0.8/\text{h}$, and ratio $\text{H}_2/\text{pyrolysis oil}$ $200\text{ dm}^3/\text{dm}^3$ [8].

The liquid catalyst is separated in a high pressure separator, cooled and analyzed.

The catalyst for catalytic cracking is synthesized at the Faculty of Physical Chemistry, Belgrade [9].

Basic physicochemical properties of the catalyst for catalytic cracking are presented in tab. 3.

Catalytic cracking of pyrolysis oil, is performed in accordance with the ASTM method D-3907-88 (MAT-test), in a stainless steel reactor under the following conditions: $T = 510\text{ }^{\circ}\text{C}$, $p = 1\text{ atm}$; space velocity of raw $\alpha = 148/\text{h}$, $m_{cat} = 5\text{ g}$, and $t_R = 5\text{ h}$.

The catalyst is activated by steam at $T = 760\text{ }^{\circ}\text{C}$ and $\alpha = 15/\text{h}$ in water steam.

Gaseous fraction and liquid product are analyzed by GC method and in accordance with the D-3907-88 degree of conversion and the yield of gasoline fraction.

The percent of formed coke at the catalyst is determined by the JUS.C.A1.050 method.

Results and discussion

The effect of the degree of purification of crude pyrolysis oil from oil shale on the content of sulphur, nitrogen and Conradson coke in the pyrolysis oil is shown in tab. 4.

Removal of coke and ash from crude pyrolysis oil leads to significant decrease in the content of sulphur and nitrogen in it.

The hydrodesulphurization and denitrogenation of oil previously purified as above described produces oil with significantly lower content of sulphur, nitrogen and Conradson coke than in the standard raw material for fluid catalytic cracking—MID WEST gas oil.

Table 2. Physicochemical properties of the catalyst for hydrodesulphurization and denitrogenation of pyrolysis oil from oil shale

Physicochemical properties	Value
USY content [wt.%]	11
NiO	10
WO ₃	24.5
Al ₂ O ₃	29.0
SiO ₂	25.5
Specific area [m ² g ⁻¹]	400
Specific volume [cm ³ g ⁻¹]	0.45
Particle size [nm]	1-2
Bulk density	0.45

Table 3. Basic physicochemical properties of the catalyst for catalytic cracking

Physicochemical properties	Value
Zeolite content [wt.%]	20
Al ₂ O ₃ [wt.%]	30
Na ₂ O ₃ [wt.%]	0.12
Specific area [m ² g ⁻¹]	250
Specific volume [cm ³ g ⁻¹]	1.35
Average diameter size [nm]	70

Table 4. The effect of the degree of purification of crude pyrolysis oil from oil shale on the content of sulphur, nitrogen and Conradson coke in pyrolysis oil

State of purification	S [wt.%]	N [wt.%]	Conradson coke [%]
Crude pyrolysis oil	2.97	2.83	2.31
Extraction of coke and ash	0.19	1.85	0.20
Extraction of coke and hydro processing	0.001	0.10	0.01
MID-WEST gas oil	1.43	0.10	0.58

The tab. 5 presents achieved degrees of conversion, yields of gasoline fraction and coke during catalytic cracking of the pyrolysis oil from the oil shale with different degrees of purification.

Table 5. Degrees of conversion, yields of gasoline fraction and coke

Stages of processing	Degree of conversion [%]	Yield of gasoline fraction [%]	Yield of coke [%]
Crude pyrolysis oil	25	30	12
Extraction of coke and ash	38	41	7
Extraction of coke and hydro processing	78	70	3
MIDWEST gas oil	75	68	3.5

As can be seen from the results presented in tab. 5, crude pyrolysis oil obtained by microwave pyrolysis from the oil shale and roughly purified pyrolysis oil (deashed and decoking) cannot be used directly for motor fuel production by catalytic cracking.

On the contrary, hydro treatments (hydrodesulphurization and denitrogenation) of the crudely purified pyrolysis oil enable extraordinary raw material for catalytic cracking of the pyrolysis oil.

The achieved degrees of conversion and yields of gasoline fraction of purified pyrolysis oil as described above are considerably higher than the ones for gasoline fraction of ordinary used raw materials for catalytic cracking, which implies new, direct process which can be applied for motor fuel production by catalytic cracking of the pyrolysis oil.

Hydrothermal liquefaction of microalgae and swine manure into biooil

Hydrothermal liquefaction of microalgae

Microalgae are diverse group of photoautotrophy microscopic tiny organisms which are able to transform light, water, and CO₂ into biomass by means of photosynthesis. For microalgae, rapid cells division and diverse metabolic routes [10] are specific.

High efficiency of light and CO₂ exploitation (ability of photosynthesis) and high speed of division of microalga presents the basis for completely new high efficiently technology for the production of cheap food and biomass.

Tab. 6 presents chemical composition of algae and of food that is most commonly used in human nutrition.

As can be seen from the results presented in tab. 6, the specific species of microalgae are characterized by extraordinary content of proteins and carbohydrates and therefore, they are

the most perspective resource of proteins and carbohydrates for human and animal nutrition, as well as for novel products of synthesis.

Table 6. Comparative presentation of chemical composition of common food and algae

	Proteins [%]	Carbohydrates [%]	Fats [%]
Meat	43	1	34
Milk	26	38	28
Rice	8	77	2
Soybean	37	30	20
Yeast	39	38	1
<i>Chlorella vulgaris</i>	51-58	12-17	14-22
<i>Porphyridium cruentua</i>	28-39	40-57	9-14
<i>Spirulina maxima</i>	60-71	13-16	6-7

Also, particular types of microalgae are characterized by high content of lipids: *Botryococcus braunii* (25-85%), *Dunaliella sp* (18-67%), *Neochloris oleoabundans* (26-70%) and so, they present the most perspective raw material for the production of fat and biodiesel [11, 12].

The conventional process of biodiesel production from bioalgae is based on the extraction of triglycerides from algae and their conversion and trans-esterification into biodiesel. Due to high water content in microalgae (90%), biomass drying is necessary before solvent extraction of triglycerides.

Both the procedure of microalgae drying and the extraction of triglycerides with organic solvents are expensive and energetically inefficient processes which are the main reasons of algae oil high price.

In order to overcome those problems, the possibilities of direct hydrothermal liquefaction of algae to biooil are investigated [13].

Materials and methods

Alga *Botryococcus braunii* strain UTEX 572 from the collection of the University of Texas from Austin is used for hydrothermal liquefaction. Algae are grown in modified Ch-13 [14] liquid medium. Algae are separated from liquid phase by filtering and washed with distilled water.

The moisture content in algae cells is determined gravimetrically by drying at 105 °C for 24 hours. The ash content is also determined gravimetrically by combustion at 600 °C during 1 hour.

Elemental analyses of algae and biooil (C, H, O, N content determination) are performed at LECO elemental analyzer model CHNS-932. Hydrothermal liquefaction of algae to biooil is performed in own reactor having volume $V = 1$ L, which I have constructed [13]. Determined algae mass (100 g) and distilled water are added to the autoclave. The autoclave is purged with N_2 , closed and adjusted to operating conditions: temperature, pressure, time.

After hydrothermal liquefaction, the autoclave is cooled. A gas fraction released from the cooled autoclave and captured in the storage container. The liquid product is filtered in order to separate solid residue. The organic phase of liquid product (biooil) is extracted by hexane.

The lower calorific value of biooil is determined by calorimetric bomb model 1351 (Parr, USA). The coefficient of viscosity of biooil is determined on Brookfield DV-1 viscometer.

Results and discussion

Basic physicochemical properties of microalgae, *Botryococcus braunii*, are presented in tab 7.

The effects of algae hydrothermal liquefaction duration on the yield of biooil ($T = 350\text{ }^{\circ}\text{C}$; $c_s = 20\%$; $p = 10\text{ MPa}$) are given in tab. 8.

Table 7. Basic physicochemical properties of the microalgae *Botryococcus braunii*

Physicochemical properties	Value
Moisture content [%]	89
Organic material content [%]	98
Ash content [%]	2
C [wt.%]	65
H [wt.%]	12
N [wt.%]	3
O [wt.%]	20
Calorific value [MJkg^{-1}]	35.8

Table 8. The effects of duration of hydrothermal liquefaction of algae on the yield of biooil

Time [minute]	Yield [wt.%]
5	14
10	20
15	30
30	28
45	26
60	20

The effect of temperature on hydrothermal liquefaction of algae on the degree of conversion and physicochemical properties of the produced biooil is presented in tab. 9 ($p = 18\text{ MPa}$, $c_s = 20\%$; $t = 15\text{ minutes}$).

Table 9. The effect of temperature on hydrothermal liquefaction of algae on the degree of conversion and physicochemical properties of the produced biooil

Properties	200 °C	250 °C	300 °C	320 °C	350 °C	5% CAT
Conversion	65	83	95	89	60	97
C [%]	77	80	85	82	83	86
H [%]	15	15	14	14	14	13.9
N [%]	0	0.5	1.0	2.5	1.5	0
O [%]	8.0	4.0	0	1.5	1.5	0
Calorific value [MJkg^{-1}]	46.3	48.1	49.1	47.8	48.12	49.3
Coefficient of viscosity 50 °C [$\text{mPa}\cdot\text{s}$]	230	78	75	76	77	65

As can be seen, when hydrothermal liquefaction takes place in time shorter than $t < 15\text{ min.}$, then the yield of biooil increases. On the contrary, for the duration of hydrothermal liquefaction higher than $t < 15\text{ min.}$, the yield of biooil decreases.

Hydrothermal liquefaction is a complex process during which celluloses, hemicelluloses, lignin, lipids, carbohydrates, and proteins transform to biooil, gaseous and solid residue.

Zhang [15] assumes that this complex process can be described by three basic stages: hydrolysis, depolymerization and repolymerization (condensation).

Bearing that in mind, the decrease in the yield of biooil with the increase in the duration of hydrothermal liquefaction, under given reaction conditions can be explained by the dominant influence of the cracking process of light hydrocarbon fraction on the reaction mechanism of hydrothermal liquefaction of algae.

At temperature range from 200 to 300 °C, the increasing temperature leads to the increasing degree of conversion, the content of C, N and calorific value while the content of H and O and the coefficient of viscosity decrease. In contrast to this, for temperatures $T \geq 300$ °C, the increasing temperature leads to the decrease in the degree of conversion and the content of C and, N, while the content of H and O is not influenced.

The established changes in the degrees of conversion of hydrothermal liquefaction and physicochemical properties of biooil are the consequence of changes in the mechanism of hydrothermal liquefaction with changes in temperature which are above all caused by the changes in ionic properties of water with temperature.

Due to that, at temperatures around 200 °C, the processes of hydrolyses of lignocelluloses materials (to monosaccharide) and proteins (to amino acids) have the dominant effects on the mechanism of hydrothermal liquefaction, At the temperature range from 200 to 300 °C, the processes of repolymerization and condensation reactions and so, the increased degree of conversion and content of C in biooil have the dominant effect on the mechanism of hydrothermal liquefaction. At temperatures $T \geq 300$ °C, the processes of decerboxilation and cracking of light carbohydrates of biooils become dominant, and due to that the decreased content of C, N and the percentage of gaseous fractions increase in biooil.

Hydrothermal liquefaction of swine manure

Since there is no organized algae production aimed at the preparation of new biosustainable fuel of third generation production in Republic of Serbia, the possibilities of getting biooil by hydrothermal liquefaction of swine manure are investigated.

Basic physicochemical properties of swine manure are presented in tab. 10.

Swine manure significantly differs from microalgae *Botryococcus braunii* in the majority of physicochemical properties. Bearing that in mind, as well as the above suggested model of the mechanism for hydrothermal liquefaction process of biomass, it should be expected that both the yield and physicochemical properties of biooils obtained from these two starting materials, *i. e.*, microalgae and swine manure, significantly differ one from the another.

The effect of the temperature of hydrothermal liquefaction process of swine manure is presented in fig. 1 ($p = 15$ MPa ; $c_s = 20\%$; $t = 15$ minutes).

Table 10. Basic physicochemical properties of swine manure used in the hydrothermal liquefaction process

Physicochemical properties	Value
Volatile compounds [%]	78
Ash content [%]	22
C [wt.%]	33.5
H [wt.%]	6.2
N [wt.%]	2.8
O [wt.%]	57.7
Calorific value [MJkg ⁻¹]	7.89

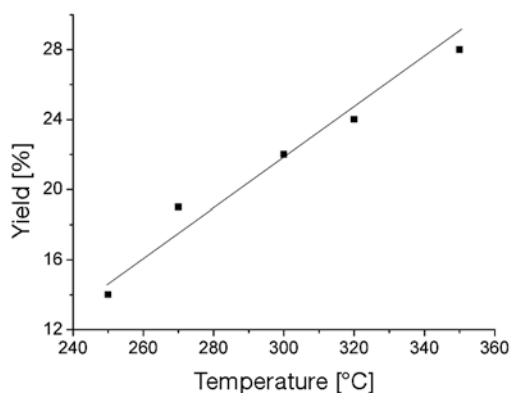


Figure 1. The effect of temperature of hydrothermal liquefaction process of swine manure

Based on results presented in fig. 1, it is easy to conclude that within the investigated temperature range, the yield of biooil linearly increases with the increased temperature.

The found changes in the yield of biooil with increasing temperature of hydrothermal liquefaction are in agreement with the above presented model for the mechanism of hydrothermal liquefaction process and with the considerable amount of fats and lignocelluloses materials in swine manure.

Table 11 presents basic physicochemical properties of standard fuels: motor gasoline (MOF), diesel (D) heating oil and biooil obtained from algae *Botryococcus braunii* (BO-1) and from swine manure (BO-2).

Table 11. Physicochemical properties of standard fuels: motor gasoline, diesel, heating oil and biooil obtained from algae *Botryococcus Braunii* and from swine manure

Property	Diesel	BO-1	BO-2	Gasoline
Elemental analysis [wt.%]				
C	87	85	72.6	86
H	12.8	14	9.8	14
N	0.01	4.5	4.5	0
O		1	13.2	0
Ash		0	0.13	0
Coefficient of viscosity 50 °C [Pa·s]	3	75	840	0.4
Calorific value [MJkg ⁻¹]	42.6	49.1	36.1	45.1

The calorific value of biooil obtained by hydrothermal liquefaction process is significantly higher than the calorific value of all other motor fuel known so far. The calorific value of biooil obtained by hydrothermal liquefaction of swine manure is comparable with that of the heating oil.

The content of nitrogen compounds and viscosity coefficient of biomass is significantly higher than their content in standard motor fuel.

Conclusions

Actual annual potentials of the Autonomous Province of Vojvodina in waste lignocelluloses materials are enough for motor fuel demand in the Autonomous Province of Vojvodina and in the Republic of Serbia.

Scientific institutions in Serbia have own, modern technologies for the productions of biofuel of the second generation.

The hydrothermal liquefaction of algae, various manures and other lignocelluloses materials, presents a new, highly effective technology for the production of biofuel of the third generation – biooil.

The development of agriculture in the Autonomous Province of Vojvodina should be redirected towards algae, yeasts and bacteria.

The coupled microwave pyrolysis of oil shale and catalytic cracking of purified pyrolysis oil present a new technology for motor gasoline production.

Significant production ($\geq 30\%$) of motor fuel from alternative materials can be achieved in short time only by using oil shale.

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