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## The improved diesel-like fuel from upgraded tire pyrolytic oil

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**Abstract:** Tire pyrolytic oil (TPO) obtained from thermal pyrolysis of scrap tires is not a diesel equivalent fuel which can be used directly in vehicles due to its high density, viscosity, sulfur content, low flash point and low cetane index. It can only be used in a limited way by mixing with diesel fuel (DF) in amounts less than 30 %. In this study, the pyrolysis of scrap tires was carried out at a heating rates of 5 and 10 °C min<sup>-1</sup> in the range of 450–600 °C, using a mixture of hierarchical zeolite (HZSM-5), mesoporous silica (MCM-41) and quicklime (CaO) as the catalyst. The obtained TPO and catalytic pyrolytic oil (CPO) were upgraded by pre-treatment, and distillation consisting of a mixture of Cu(I)-loaded mesoporous aluminosilicate (Cu(I)-MAS) and MCM-41, desulfurization and decolorization steps, respectively. To obtain diesel-like fuel, the upgraded catalytic pyrolytic oil (UCPO) and biodiesel (PBD) obtained from palm oil were blended in certain proportions. Density, viscosity, flash point and cetane index of the obtained diesel-like fuels were found within the limit values of diesel fuel.

**Keywords:** desulfurization; mesoporous zeolite; microporous zeolite; catalytic pyrolysis; thermal pyrolysis.

### INTRODUCTION

The amount of tires produced worldwide is over 1.5 billion tons, expired tires are replaced with new ones and stored as scrap or waste.<sup>1,2</sup> The rain water, which accumulates on the surfaces and interiors of scrap tires which are left indiscriminately in the environment becomes center of biological life for pests such as bacteria and harmful insects. Scrap tires released into the environment are dangerous for human life and cause the spreading of infectious diseases. Tire management systems have been established and action plans have been prepared to combat scrap tires in developed countries.<sup>3,4</sup> Today, five different methods in waste management draw attention to prevent waste tires from accumulating in

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the environment. These encompass: *i*) reduction, improving the physicochemical methods used in tire manufacture to increase tire life;<sup>5,6</sup> *ii*) reuse of tires by coating or production of raw materials from tires by chemical or thermochemical methods;<sup>7-9</sup> *iii*) recovery, direct burning of tires as an energy source;<sup>10,11</sup> *iv*) recycling, mechanical recovery to produce industrial material (ground rubber), or thermal recovery to obtain fuel;<sup>12,13</sup> *v*) regulation, landfill of tires.<sup>14,15</sup>

All these solution methods still have not reached the capacity to reduce the amount of scrap tire accumulation. The most striking of these methods is the pyrolysis method of scrap tires, which is among the recycling methods. High market demand fuel and pyrolytic carbon black are produced in the pyrolysis method. However, low quality pyrolytic oils and pyrolytic carbon black obtained by pyrolysis of scrap tires are not yet suitable for market demand.<sup>16</sup> Therefore, improving the quality of the products obtained from pyrolysis in a way that will respond to the market demand will pave the way for recycling methods, reduce the amount of scrap tire accumulation and will be a prominent action plan in tire management systems.

The endothermic thermal decomposition process in which rubber, plastic, coal, heavy oils and similar hydrocarbons transform into solid residue (pyrolytic carbon black), liquid oil (pyrolytic oil) and combustible gases (pyrolytic gas) in an oxygen-free environment at high temperatures is called pyrolysis.<sup>17</sup> In general, 40–55 % pyrolytic oil (TPO), 30–40 % pyrolytic carbon black (pCb) and 10–20 % pyrolytic gases are obtained from the pyrolysis of scrap tires. In the pyrolysis process, variables such as reactor type, temperature, heating rate, catalyst, retention time, feed size of the raw material and flow rate of the carrier inert gas are the most important factors that determine the yield, physical and chemical structure of pyrolytic products.

#### *Pyrolysis process of waste tire*

Al-Saleh<sup>18</sup> and Aylon<sup>19</sup> comparatively explained that fixed bed reactors (FBR), rotary kiln reactors and fluidized bed reactors are the most commonly used reactor models for the pyrolysis of scrap tires. Fixed bed reactors are slow pyrolysis model with long residence time (minutes to hours) and low heating rate. Since there is no mixing, homogeneous heat distribution and homogeneous catalyst distribution cannot be achieved in the reactor. Tire processing capacity is low due to the problem of heat transfer to the inner parts of the reactor. Since mechanical problems are experienced due to rubber wires in stirred FBR reactors, it is not preferred in applications. Although the heat and catalyst mix homogeneously in the rotary kiln reactors, the rubber processing capacity is limited due to the high bulk volume of the tires. In continuous rotary reactors, additional processing costs are incurred due to the small tire size loading requirement. Fluidized bed reactors are known as flash pyrolysis and the retention time is in the

order of seconds. However, since it requires tires in the form of granules with a high surface area and the rubber feed rate to the reactor is lower than the heating fluid. In order to achieve high tire processing capacity, it is necessary to set up very large volume processes. Therefore, fluidized bed reactors are generally in the form of pilot plants with a tire feeding capacity of 200 kg h<sup>-1</sup>. Thermal conversion rates of tires are close to each other in fluidized bed reactors and fixed-bed reactors. The only difference in reactor types is that the retention and pyrolysis times are longer in the fixed bed reactor.

The effects of temperature,<sup>18–22</sup> heating rate,<sup>23–26</sup> catalyst<sup>27–34</sup> and fuel blends<sup>35,36</sup> on pyrolysis process are discussed in details in the Supplementary material to this paper.

In this study, pyrolytic oils were obtained from thermal and catalytic pyrolysis of tires in a fixed bed reactor at atmospheric pressure, in the range of 450 to 600 °C. Density, viscosity, flash point and cetane index of the obtained pyrolytic oil were upgraded by catalytic distillation and desulfurization methods. By blending the upgraded pyrolytic oil and biodiesel with high flash point and cetane indices obtained from palm oil in a wide range, a fuel with physical properties very similar to diesel was obtained.

#### EXPERIMENTAL

Cetyltrimethylammonium bromide (CTMAB, 98 %) and sodium aluminate (NaAlO<sub>2</sub>) obtained from Sigma–Aldrich, nanocluster zeolite Y (NaY) and HZSM-5 obtained from Julong Chemical Co., China, sodium silicate solution (8 % Na<sub>2</sub>O, 27 % SiO<sub>2</sub>), CaO obtained from the local market, polyacrylamide (av. *MW* 150.000), H<sub>2</sub>SO<sub>4</sub> (97 %), NaOH, Cu(NO<sub>3</sub>)<sub>2</sub> and silica gel (particle size 63–200 μm, pore size 6 nm (0.7–0.85 cm<sup>3</sup> g<sup>-1</sup> pore volume, surface area ≥ 480 m<sup>2</sup> g<sup>-1</sup>) was obtained from Merck company. Waste tires obtained from local recycling firms as 5–10 mm sizes. Leco, CHNS-932 elemental analyzer was used for C, H, N, S analysis in fuel. Viscosity measurements were made according to the ASTM D445 method. The Ostwald viscometer was filled with the pyrolytic oil sample and kept in a water bath at a constant temperature of 40 °C for 30 min. Then, the flow time between the two marked lines was measured with a stopwatch. The kinematic viscosity of the oil was calculated by considering the flow time and the viscometer calibration constant. The calorific value of the pyrolysis oil samples was measured using a U-Therm YX-ZR model semi-automatic calorimeter according to ASTM D240-09 method. Densities of pyrolytic oils were measured with Anton Paar DMA 38N density meter according to the ASTM D7777 method. The flash point of the pyrolytic oil samples was determined using the PMA 500 model Pensky–Martens device according to the ASTM D93 method.

##### *Mesoporous MCM-41 synthesis*

MCM-41 was synthesized according to the method in the literature.<sup>37</sup> CTMAB (7.22 g) was dissolved in 100 cm<sup>3</sup> distilled water, sodium silicate (26.52 g) was added dropwise to the solution while stirring. H<sub>2</sub>SO<sub>4</sub> was added dropwise to the solution until the pH was 11.0. The mixture was allowed to heat in an oven at 100 °C for 24 h. The precipitate was filtered, washed, and dried at 55 °C under vacuum, before calcination. The dried precipitate was calcined at 550 °C with a heating rate of 2 °C min<sup>-1</sup> for 6 h.

*Mesoporous aluminosilicate (MAS) synthesis*

MAS was synthesized by two-step method.<sup>33</sup> Nanocluster zeolite Y seeds (NaY) were prepared through the reaction of NaOH (0.088 mol) and NaAlO<sub>2</sub> (0.10 mol) in H<sub>2</sub>O (8.5 mol) with silicate anions (0.9 mol) in the form of sodium silicate solution. The solution was aged overnight. Then, the seed solution was added to CTMAB (0.27 mol) solution. The pH value was lowered to 10 with sulfuric acid. The mixture was placed at 100 °C for 24 h. The as-synthesized MAS was calcined under nitrogen atmosphere at 550 °C for 1 h, and then in the air at the same temperature for 6 h.

*Cu(I)-MAS synthesis*

Cu(I)-MAS was synthesized according to the method in the literature.<sup>33</sup> Ion exchange was performed by mixing MAS with 0.5 M Cu(NO<sub>3</sub>)<sub>2</sub> solution for 24 h. Then, the filtered adsorbent was dried at 100 °C for 24 h. Finally, Cu<sup>+2</sup> was reduced to Cu<sup>+</sup> by calcining in a nitrogen atmosphere at 450 °C for 3 h.

*Pyrolysis experiment*

Pyrolysis experiments were carried out in an apparatus consisting of a fixed-bed reactor, condenser, and desulfurization equipment of non-condensed gases. The fixed-bed reactor with a diameter of 100 mm and a height of 200 mm is made of 2 mm stainless steel and a 4 kW electric heater is mounted. The reactor was isolated by wrapping it with silica wool. Temperature and pressure in the reactor were controlled by PID. A tube bundle condenser with a length of 700 mm and a diameter of 100 mm was used to condense and separate the pyrolytic gases. The non-condensed gases were desulfurized by passing through a container with a basic solution and burned directly. The pyrolysis process was carried out at atmospheric pressure using inert N<sub>2</sub> carrier gas (a flow rate of 5 L min<sup>-1</sup>). The scrap tire composition used is given in Table I. Shredded tire pieces and catalyst (40 wt.% HZSM-5 + 40 wt.% MCM-41 + 10 wt.% CaO) were put into the reactor and the pyrolysis was carried out at 450, 500, 550 and 600 °C with different heating rate. The pyrolytic gases were cooled by passing through the heat exchanger and the pyrolytic liquid products were collected in a collection vessel, the non-condensed gases were burned by passing through a solution containing 4 M NaOH. In the pyrolysis experiment, yields were calculated from the amount of pyrolytic liquid and the amount of carbon black remaining in the reactor. The amount of gas was calculated as the remaining balance from the sum of pyrolytic oil and carbon black:

$$\text{Content of pyrolytic oil, wt.\%} = 100(\text{Pyrolytic oil weight}/\text{Total tire weight}) \quad (1)$$

$$\text{Pyrolytic gas weight} = \text{Waste tire weight} - (\text{pyrolytic oil weight} + \text{pCB weight}) \quad (2)$$

TABLE I. Waste tire composition

Ultimate analysis	Content, wt. %
C	86
H	8
N	1
S	2
Proximate analysis	
Volatiles	62
Fixed carbon	30
Ash	7
Moistures	1

### *Upgrade of pyrolytic oils (UTPO)*

Refinement of pyrolytic oils consists of pretreatment, atmospheric distillation, desulfurization and decolourization, respectively.<sup>38</sup>

#### *Pre-treatment and settling of sludge*

The precipitation of undesirable components such as water and tar from the pyrolytic oil was carried out according to the methods in the literature.<sup>39,40</sup> The pyrolytic oil and a flocculant/coagulant containing 0.2 wt. % polyacrylamide and 0.5 wt. % sodium silicate was mixed with an air compressor at 60 °C for 2 h, then left for 6 h to precipitate the asphaltenes. Thus, the residue and water were separated from the pyrolytic oil.

#### *Distillation*

Some 600 cm<sup>3</sup> of the supernatant were placed in a packed column-mounted distillation kettle. The filled column mounted on the distillation kettle has a diameter of 32 mm and a height of 400 mm. Ceramic wool was placed at the bottom of the column and zeolite adsorbent (50 % Cu(I)-MAS + 50 % MCM-41) was filled on the column. The distillates were collected in the collection vessels between 55 and 360 °C. The non-condensed gases were burned in the burner after desulphurization by passing from a 4 M NaOH solution.

#### *Desulfurization and decolourization process*

Oxidative desulfurization experiments of pyrolytic oils were carried out according to the method in the literature.<sup>39</sup> Distilled pyrolytic oil (100 cm<sup>3</sup>), 3 cm<sup>3</sup> of 30 % by weight H<sub>2</sub>O<sub>2</sub>, 5 cm<sup>3</sup> deionized water, 4 cm<sup>3</sup> formic acid and 0.7 g activated carbon were mixture in 250 cm<sup>3</sup> of a beaker with a mechanical stirrer (100 rpm) at 60 °C for 60 min. At the end of the reaction, the oxidized oil separated from the mixture was washed with 50 cm<sup>3</sup> of 5 % by weight sodium carbonate solution and dried over anhydrous sodium sulphate. The pyrolytic oil obtained after drying was mixed with 2 % silica gel at 60 °C for 1 h, the sulphur and impurities remaining in the oil were adsorbed, its colour was lightened and filtered as upgraded tire pyrolytic oil.

#### *Synthesized palm oil biodiesel (PBD)*

Biodiesel from palm oil is synthesized according to the method in the literature.<sup>41</sup> Palm oil was mixed with solution of 0.3 % NaOH in 6:1 ratio of methanol. The mixture was stirred at 600 rpm for 4 h by heating at 64 °C below the boiling point of methanol, 65 °C, to prevent methanol evaporation. The solution was left overnight to separate the glycerine from the synthesized biodiesel mixture. The solution was left overnight to separate the glycerine from the synthesized biodiesel mixture. The glycerine phase was separated from the biodiesel phase, the biodiesel phase was heated up to 80 °C and excess methanol was evaporated. After the solution was washed 3 times with deionized water at 45 °C, excess water was removed from the biodiesel by evaporation at 110 °C. The obtained biodiesel was mixed with 1 wt. % silica gel for 1 h at 60 °C and filtered. The obtained PBD was mixed with the UTPO in certain proportions to obtain fuel blends.

## RESULTS AND DISCUSSION

Purification of pyrolytic oils consists of desulphurization and decolorization stages of distilled pyrolytic oil, after the separation of tar and heavy phases by distillation method. Even if pyrolytic fuels are upgraded by distillation and desulphurization method, combustion problems continue in diesel engines due to their low cetane index and low flash point.<sup>42</sup>

In this study, the improvement of pyrolytic oil was started at the pyrolysis stage. With catalytic pyrolysis, the physical properties of crude pyrolytic oil have been improved compared to the pyrolysis method without catalyst. After the pyrolysis step, the pyrolytic oil was upgraded by catalytic distillation and desulfurization method. Finally, palm oil was blended with biodiesel to improve its physical properties such as viscosity, flash point and cetane index to obtain diesel-like fuel. Thus, pyrolytic oils have reached a more economical, sustainable alternative energy quality in diesel engines with more problem-free combustion properties, and are intended to be blended with a more environmentally friendly second fuel at high rates without the need for a limited blending with diesel fuel.

Thermal pyrolytic oil (TPO) and catalytic pyrolytic oil (CPO) were obtained from thermal and catalytic pyrolysis of scrap tires using 1 and 2 % catalysts, at 450–600 °C with heating rates of 5 and 10 °C min<sup>-1</sup>. TPO and CPO were upgraded with catalytic distillation, desulfurization and decolourization methods to obtain upgraded thermal pyrolytic oil (UTPO) and upgraded catalytic pyrolytic oil (UCPO). As an exemplary study, UCPO at 600 °C with a heating rate of 5 °C min<sup>-1</sup> and PBD were blended in different mixing ratios to obtain diesel-like fuel. Since the pyrolysis experiments were carried out in a fixed-bed reactor, at constant inert nitrogen gas flow, with equivalent tire sizes, other variables such as: temperature, heating rate, the effect of the catalyst, which are other factors affecting pyrolysis, are explained below. In this study, since it is aimed to obtain diesel-like fuel from pyrolytic oils, carbon black and pyrolytic gases are not emphasized.

#### *Pyrolysis process of waste tire*

In order to study the effects of temperature and catalyst on pyrolysis in laboratory-scale experiments, the fixed-bed reactor type is more suitable and more practical to set up. In this study, an industrially applicable fixed-bed pyrolysis method was used in pyrolysis experiments. In order to obtain a larger heating surface area, the pyrolysis process was carried out in a horizontal reactor, since the carbon black deposited at the bottom of the vertical reactors makes heat transfer difficult and the bottom of the reactor has a low surface area. Thus, not only is heat transfer improved, but the retention times of cracked molecules are reduced. The empty volume of pyrolysis reactor (the 10 cm diameter and 20 cm length) used in the experiments is 1.570 g cm<sup>-3</sup>. The bulk volume of 5–10 mm sized tire pieces<sup>43</sup> is 0.546 g cm<sup>-3</sup>, and theoretically 0.857 g of rubber pieces can be filled into the reactor according to the 100 % filling rate. In the experiments, 25–30 vol. % of rubber pieces was filled into the reactor. The pyrolysis experiments were carried at atmospheric pressure, using inert carrier N<sub>2</sub> gas at a flow rate of 5 L min<sup>-1</sup>. The main variables are temperature, heating rate and amount of catalyst at pyrolysis experiments. Since the combination of microporous and mesoporous

zeolite is used in the pyrolysis process, although the thermal decomposition rate is high, secondary reactions are minimized with mesoporous MCM-41 and carrier nitrogen gas.

### Temperature

Thermocatalytic degradation of polymers is faster at high temperatures. At higher temperatures, the residence time is shorter in the polymer phase, and secondary reactions occur in the vapor phase. Therefore, as the polymer breaks down into smaller molecules and the gasification rate increases, pyrolytic oil yield and fuel quality increase. As the components decompose at high temperatures, undesirable components such as sulphur, residual carbon, moisture and ash will be reduced and the quality of pyrolytic products (carbon black and pyrolytic oil) will increase.<sup>44,45</sup>

As it can be seen in Fig. 1, the pyrolytic oil yield increased up to 500 °C and decreased between 500 and 600 °C. The Fig. 2 shows that the pyrolytic gas yield increases regularly from 450 to 600 °C. There is no significant deviation in the carbon black yield, the carbon black amount is within the expected values. In the pyrolysis experiments, the lowest amount of pyrolytic oil was obtained at 600 °C, at 10 °C min<sup>-1</sup> heating rate, and the highest amount of pyrolytic oil was obtained at 450 °C, at 5 °C min<sup>-1</sup> heating rate.

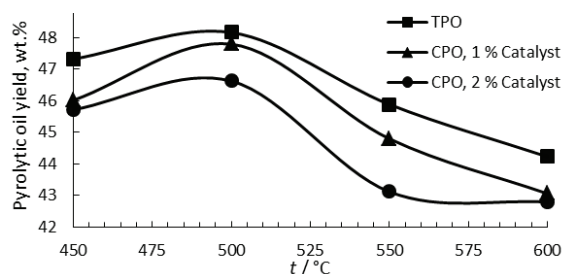


Fig. 1. The relationship of pyrolytic oil yield from catalytic pyrolysis and thermal pyrolysis with temperature, heating rate of 5 °C min<sup>-1</sup>.

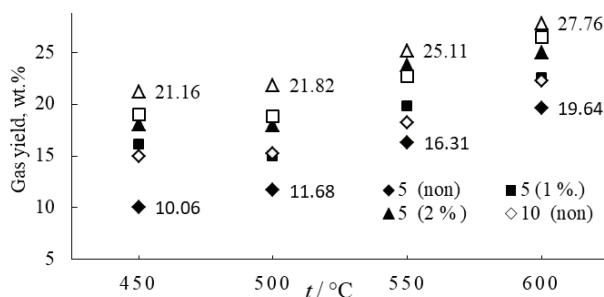


Fig. 2. The amount of pyrolytic gas obtained from pyrolysis between 450–600 °C, heating rate of 5 and 10 °C min<sup>-1</sup>, with 1 and 2 % catalyst.

The retention time in the polymer phase is longer at 450 °C. The highest pyrolytic carbon black was obtained from thermal pyrolysis at 450 °C, 42.62 % (Fig. 3). In the experiments carried out with 2 % catalyst and 10 °C min<sup>-1</sup> heating rate, it is seen that carbon black decreases from 34.36 to 32.46 % levels at 500 °C. As can be understood from here, the thermal degradation of the polymer reached its maximum level up to 500 °C. While the change in the amount of carbon black decreased after 500 °C, gas formation continued to increase. As it can see in Tables II–IV, although the pyrolytic oil yield is higher at low temperatures, the physical properties of pyrolytic oil are closer to high-temperature diesel fuel. In pyrolysis processes, it is desirable to obtain higher quality pyrolytic oil instead of high efficiency. For this reason, high pyrolysis temperature should be preferred to obtain diesel-like fuel.

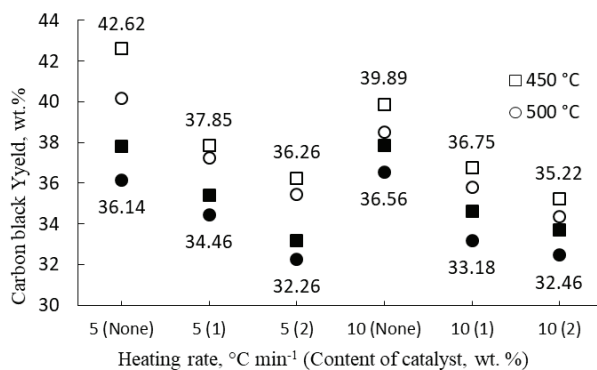


Fig. 3. The amount of pyrolytic carbon black obtained from pyrolysis between 450 and 600 °C, heating rate of 5 and 10 °C min<sup>-1</sup>, with 1 and 2 % of catalyst.

TABLE II. Physicochemical properties of pyrolytic oil (TPO) and upgraded pyrolytic oil (UTPO) obtained from thermal pyrolysis at different temperatures

Pyrolytic oil properties	<i>t</i> / °C							
	450	500	550	600	450	500	550	600
	TPO				UTPO			
C content, wt. %	84.56	84.60	84.89	85.38	86.43	86.34	86.65	87.30
H content, wt. %	10.92	10.89	10.79	10.48	11.14	11.11	11.01	10.69
N content, wt. %	0.87	0.92	0.98	1.29	0.26	0.28	0.29	0.39
S content, wt. %	1.83	1.62	1.59	1.51	0.37	0.32	0.32	0.30
Ash content, wt. %	1.82	1.97	1.75	1.34	1.80	1.95	1.73	1.33
Moisture content, wt. %	5.93	5.71	4.62	4.27	0.30	0.29	0.23	0.21
Content of residue carbon, wt. %	2.47	2.11	1.89	1.82	0.25	0.21	0.19	0.18
<i>GCV</i> <sup>a</sup> / MJ kg <sup>-1</sup>	40.18	40.91	41.71	42.16	42.19	42.96	43.80	44.27
Density, kg m <sup>-3</sup>	920.74	915.27	905.45	895.18	874.70	869.51	860.18	850.42
$\nu^b$ / cSt at 40 °C	5.97	5.76	5.22	4.36	3.87	3.62	3.32	2.84
Flash point, °C	36.00	34.00	33.00	29.00s	37.08	35.02	33.99	29.87

<sup>a</sup>Gross calorific value; <sup>b</sup>kinematic viscosity



TABLE III. Physicochemical properties of catalytic tire pyrolytic oil (CPO) and upgraded catalytic pyrolytic oil (UCPO) with 1 wt. % of catalyst

Pyrolytic oil properties	<i>t</i> / °C							
	450	500	550	600	450	500	550	600
	CPO with 1 % catalyst				UCPO with 1 % catalyst			
C content, wt. %	84.62	84.67	84.95	85.42	86.41	86.34	86.63	87.25
H content, wt. %	11.14	11.11	11.01	10.69	11.36	11.33	11.23	10.90
N content, wt. %	0.83	0.87	0.93	1.23	0.25	0.26	0.28	0.37
S content, wt. %	1.78	1.57	1.54	1.46	0.36	0.31	0.31	0.29
Ash content, wt. %	1.64	1.77	1.58	1.21	1.62	1.76	1.56	1.19
Moisture content, wt. %	3.56	3.43	2.77	2.56	0.18	0.17	0.14	0.13
Content of residue carbon, wt. %	1.98	1.69	1.51	1.46	0.20	0.17	0.15	0.15
<i>GCV</i> <sup>a</sup> / MJ kg <sup>-1</sup>	41.39	42.14	42.96	43.42	43.45	43.40	44.25	44.73
Density, kg m <sup>-3</sup>	856.29	851.20	842.07	832.52	847.73	842.69	833.65	824.19
$\nu^b$ / cSt at 40 °C	5.55	5.04	4.85	3.99	3.42	3.21	2.74	2.18
Flash point, °C	36.36	34.34	33.33	29.29	37.45	35.37	34.33	30.17

<sup>a</sup>Gross calorific value; <sup>b</sup>kinematic viscosity

TABLE IV. Physicochemical properties of catalytic tire pyrolytic oil (CPO) and upgraded catalytic pyrolytic oil (UCPO) with 2 wt. % of catalyst

Content of pyrolytic oil	<i>t</i> / °C							
	450	500	550	600	450	500	550	600
	CPO with 2 % catalyst				UCPO with 2 % catalyst			
C content, wt %	85.73	85.95	86.34	86.99	87.34	87.64	88.00	88.67
H content, wt %	10.84	10.79	10.74	10.13	10.95	10.90	10.85	10.23
N content, wt %	0.57	0.76	0.81	0.93	0.17	0.23	0.24	0.28
S content, wt %	1.64	1.57	1.49	1.41	0.33	0.31	0.30	0.28
Ash content, wt. %	1.22	0.93	0.62	0.54	1.21	0.92	0.61	0.53
Moisture content, wt. %	3.20	3.08	2.49	2.31	0.16	0.15	0.12	0.12
Content of residue carbon, wt.%	1.78	1.52	1.36	1.31	0.18	0.15	0.14	0.13
<i>GCV</i> <sup>a</sup> / MJ kg <sup>-1</sup>	40.82	41.47	42.11	43.12	42.04	42.71	43.37	44.41
Density, kg m <sup>-3</sup>	858.71	852.14	848.43	842.11	850.12	843.62	839.95	833.69
$\nu^b$ / cSt at 40 °C	4.92	4.62	4.32	3.76	3.57	3.46	3.22	2.57
Flash point, °C	36.54	34.51	33.50	29.44	37.64	35.55	34.50	30.32

<sup>a</sup>Gross calorific value; <sup>b</sup>kinematic viscosity

As it can be seen in Tables II–IV, in the thermal pyrolysis and catalytic pyrolysis experiments between 450 and 600 °C, a decrease was observed in parameters which decrease fuel quality such as sulphur value, ash, residual carbon, and moisture with an increase in temperature. Gross calorific value of pyrolytic oils increased, viscosity, density and flash point decreased. It can be seen that there is an improvement in the physical properties of the oil at high temperature.

#### Heating rate

As the heating rate increases, the density and efficiency of the pyrolytic oil decrease as a result of the increase in secondary reactions, since the retention

time in the vapor phase is prolonged. As the retention time of cracked molecules decreases, secondary reactions such as secondary repolymerization and isomerization decrease. As the heating rate decreases, the retention time in the polymer phase increases and the density of the pyrolytic oil, tar formation, coking increases, and the pyrolytic oil yield increases.

In this study, as it can be seen in Fig. 1, the highest pyrolytic oil yield was obtained from thermal pyrolysis, similar to the results found by the researchers. As the temperature increased, maximum oil yield was obtained at 500 °C, and pyrolytic oil yield decreased after 500 °C. Figs. 1 and 2 clearly show that the optimum pyrolysis temperature is 500 °C to obtain the highest amount of pyrolytic oil, and secondary reactions (gasification) increase in the range of 450–600 °C. The lowest pyrolytic oil was obtained at 600 °C, with a heating rate of 10 °C min<sup>-1</sup>. As it can be seen in Tables III and IV, although the pyrolytic oil obtained from pyrolysis without catalyst has the highest efficiency, the physical properties of the fuel obtained from the catalytic pyrolysis experiments are closer to diesel fuel.

#### *Catalyst*

Microporous HZSM-5 and mesoporous ZSM-5, whose pore diameter is smaller than MCM-41, increase the gasification rate by converting molecules into smaller molecules by vapor phase secondary reactions. Although MCM-41 has the ideal pore size to break up large molecules, it is easily deactivated due to its weak acidic structure and large pore volume. For these reasons, mesoporous and microporous catalyst combinations were preferred to obtain better fuel quality pyrolytic products such as diesel and kerosene by minimizing the gasification rate, taking into account the prolongation of the retention time in the vapor phase depending on the temperature increase in the catalytic cracking experiments.

In this study, a mixture of 40 % HZSM-5 + 40 % MCM-41 + 10 % CaO was used as a catalyst in pyrolysis experiments. The thermal cracking rate of HZSM-5 is higher than MCM-41. The use of HZSM-5 alone increases the amount of uncondensed gas. Therefore, HZSM-5 and MCM-41 were mixed in equivalent ratios to reduce the amount of non-condensable gas and increase the pyrolytic oil yield. The amount of aromatic components was reduced by adding basic CaO to the catalyst mixture.<sup>46</sup> It was observed that 1 and 2 % catalyst amount was sufficient for thermal cracking of the tires.

#### *Upgrading of thermal and catalytic pyrolytic oil*

Thermal and catalytic pyrolytic oils have been upgraded through pretreatment, distillation, desulphurization and decolourization steps. The results from Tables II–IV show the physical properties of pyrolytic oil and upgraded pyrolytic oil obtained from pyrolysis experiments without catalyst, using 1 % catalyst and 2 % catalyst, respectively. Ash, moisture and residual carbon content of pyrolytic oils decrease with increasing temperature. As the pyrolysis temperature inc-

reased, the impurities were minimized, and the fuel quality was improved by distillation of the pyrolytic oil. The impurities reached the lowest value in the obtained pyrolytic oils at 600 °C. The carbon content of pyrolytic oil and upgraded pyrolytic oil increases as the temperature increases. The higher the carbon content of the fuel is, the higher is the gross calorific value. As the nitrogen value is improved in the upgraded pyrolytic fuels, lower NO<sub>x</sub> emissions occur.

As it can be seen in Table II, the physical properties of TPO and upgraded thermal pyrolytic oil (UTPO) are incompatible with diesel fuel, since thermal pyrolytic oil has high density and viscosity, low flash point and cetane index (*CI*). In order to obtain a diesel-like fuel, the TPO must be upgraded and blended with biodiesel derived from palm oil or animal fats (*CI* > 70)<sup>47</sup> with a high cetane index and flash point.

UCPO obtained by catalytic pyrolysis method has better fuel properties than upgraded thermal pyrolytic oil, the results are given in Tables III and IV. Density and viscosity of UCPO were lower than CPO and closer to conventional DF values. The flash point and the cetane index are the two most important factors preventing the direct use of UCPO in vehicles. Pyrolytic oil has a low flash point and low cetane index due to its high aromatic content. Mixing pyrolytic oils directly with diesel fuel in limited proportion is insufficient to solve the problems. However, it seems that the problem is solved with UCPO and PBD mixtures at higher ratios than diesel fuel.

As it can be seen from the results of the sample study shown in Table V, the cetane index, density, viscosity, flash point and calorific values of the fuel blends of UCPO and PBD were significantly improved. The resulting blended fuel is a diesel-like fuel and can be used directly as a diesel equivalent fuel by adding engine preservatives and combustion-improving additives.<sup>48</sup>

TABLE V. Physicochemical properties of upgraded catalytic pyrolytic oil (UCPO), palm oil biodiesel (PBD), blends of UCPO with PBD, and comparison with diesel fuel (DF); content of catalyst is 2 wt. %, pyrolysis temperature is 600 °C. The heating rate is 5 °C min<sup>-1</sup>

Properties	PBD	UCPO	UCPO 10	UCPO 20	UCPO 30	UCPO 40	UCPO 50	UCPO 60	DF
Density, kg m <sup>-3</sup>	861	834	858	839	852	844	847	848	830
Flash point, °C	168	30	154	55	124	83	95	104	55
Viscosity, cSt at 40 °C	4.92	2.57	4.69	2.99	4.18	3.47	3.68	3.82	2.54
<i>GCV</i> / MJ kg <sup>-1</sup>	39	44	40	43	41	42	42	42	44.83
Iodine number, mg I <sub>2</sub> g <sup>-1</sup>	47	13	43	19	36	26	29	31	1.98
Cetane index	59	37	57	41	52	45	47	49	46.5
pH	7.11	5.32	6.93	5.64	6.54	6.00	6.17	6.27	5.4
Distillation									
<i>t</i> <sub>10</sub> % recovery / °C	330	96							240
<i>t</i> <sub>50</sub> % recovery / °C	342	220							278
<i>t</i> <sub>90</sub> % recovery / °C	360	350							330

It is clear from all these results that density, viscosity, flash point and cetane index must be optimized to convert pyrolytic oils into a diesel-like fuel. In the experiments performed with 1 % catalyst in Table III, it can be seen that the density and viscosity are slightly different from diesel fuel at 450 °C, and the upgraded pyrolytic oils obtained at other temperatures are more suitable for blending with palm biodiesel. In Table IV, in the experiments performed with 2 % catalyst, it was observed that the density and viscosity values of the upgraded pyrolytic oil were slightly higher than in the experiments performed with 1 % catalyst. Similar to UCPO and PBD blends obtained at 600 °C with 2 % catalyst, biodiesel blends of upgraded catalytic pyrolytic oils obtained at 450–600 °C using 1 or 2 % catalyst are also diesel-like fuels. However, mixing ratios should be determined in accordance with diesel fuels by considering density, viscosity, flash point and cetane index in blended fuels.

#### *Pre-treatment*

Before distillation, water and asphaltenes in the pyrolytic oil were precipitated and separated from the pyrolytic oil with the help of coagulators. Polyacrylamide, which is effective at 60 °C, was chosen as the coagulant.<sup>39</sup> Sodium silicates have been used to increase the precipitation rate and to disperse water and asphaltenes.<sup>40</sup> Compared to sulfuric acid, material loss is less, takes a shorter time, and the coking problems caused by metallic impurities and asphaltenes in distillation are minimized.

#### *Distillation*

The crude pyrolytic oil separated from water, metallic impurities and asphaltenes as a result of pre-treatment were distilled between 50 and 350 °C in a column-filled distillation apparatus containing the mixture of 50 % Cu-MAS + + 50 % MCM-41 as the catalyst. The molecular sieve not only separates sulphur-containing mercaptans from the fuel in the vapour phase but also removes reduced branched structures or unwanted high molecular structures. As it can be seen in Tables II–IV, a fuel with much better physical values were obtained as a result of desulfurization and decolourization after distillation.

The distillation of crude pyrolytic oil in a single fraction increases the amount of fuel suitable for the purpose due to all fractions of pyrolytic oils having a high aromatic structure, low cetane index and low flash point. In this study, pyrolytic oils were distilled at between 50 and 350 °C without fractionation to obtain a single-phase distillate. As it can be seen in Table V, although the physical properties of pyrolytic oil and distillates obtained from thermal and catalytic pyrolysis seem suitable for diesel-like fuel, it is not a suitable fuel that can be used instead of diesel due to low flash point and low cetane index. Therefore, TPO, CPO or UCPO cause noise, knocking and high emissions of particulate matter in diesel engines.<sup>49</sup> To obtain diesel-like fuel, it is necessary to increase the flash

point and cetane index by reducing the amount of aromatic component in pyrolytic oil. The best method to solve these problems is to add other hydrocarbons to the pyrolytic oil, which improve the physical properties of pyrolytic oils, do not increase the cost of the fuel, and provide the physical properties of diesel fuel. The flash point of biodiesel (PBD) obtained from palm oil is 127 °C and its cetane index is 62, which makes it an environmentally friendly, economical diesel equivalent fuel. Blending pyrolytic oil and biodiesel solves the problems related to flash point and cetane index. As it can be seen in Table V, the physical properties of the fuel blends obtained from the mixture of improved pyrolytic oil and biodiesel at a ratio of 10–90 % are similar to conventional diesel fuel.

#### *Desulfurization and decolourization mesoporous*

In this study, crude pyrolytic oil was distilled using 50 wt.% Cu(I)-MAS + 50 wt. % MCM-41 filled catalytic packed column. Then, sulphur was removed from the pyrolytic oils by the H<sub>2</sub>O<sub>2</sub>-formic acid desulphurization method. As a result of this combination, the sulphur values of the pyrolytic oil were significantly reduced. As it can be seen in Tables II–IV, after distillation, the sulphur value decreased from 1.49 to 0.28 % as a result of desulphurization. The sulphur content in the distilled pyrolytic oil was 81 % removed. It has been understood that the catalytic tower plays an important role in desulfurization.

The silica gel added in the last step of the desulfurization process adsorbed both the remaining sulphur and the impurities. The colour of the distillates obtained from the packed column is orange–yellow. After treating the distillate with silica gel, the colour of the upgraded oil changed to lemon yellow. Since the oxidation stability of the upgraded pyrolytic oil is high, no colour change was observed for up to 15 days.

#### *Blending of UCPO and PBD to diesel-like fuel*

As a case study, fuel blends were obtained from mixtures of different ratios of PBD and UCPO (2 % of catalyst at 600 °C). In order to use the pyrolytic oil more efficiently, it is completely distilled as a single phase. The problems caused by the low cetane index and flash point of the upgraded pyrolytic fuel were resolved by blending UCPO and PBD. Thus, the fuel obtained by blending UCPO and PBD can be used directly as diesel-like fuel without the need to add diesel fuel. In addition, a much more economical and useful blended fuel derivative has been obtained since a high percentage of UCPO can be used in the blended fuel.

#### *Physicochemical properties of pyrolytic oil*

Important parameters determining the properties of pyrolytic oils, upgraded pyrolytic oils and blended fuels<sup>50–59</sup> are explained separately in details in the Supplementary material.

## CONCLUSION

The resources of fossil fuels, which constitute the majority of the world's energy needs, are decreasing day by day. In this study, a new method is presented, namely the use, as diesel fuel, of the pyrolytic oils obtained from the recycling of environmentally hazardous scrap tires by pyrolysis method. While a certain fraction of pyrolytic oil was blended with diesel fuels in a limited way, alternative uses for the majority of them contained uncertainties. In this study, it has been demonstrated that distilled pyrolytic oil obtained as a result of single-phase distillation of pyrolytic oils can be mixed with palm oil biodiesel, at a ratio of 1:1 or more, in order to obtain an edible and sustainable fuel which would be an alternative to diesel fuels. In this respect, in scrape tire pyrolysis plants, a study was carried out to support the recycling of scrap tires by pyrolysis method within the waste management plans by avoiding the uncertainties regarding the usage areas of pyrolytic oils. Since the sludge remaining from the distillation of pyrolytic oils is a high-viscosity aromatic-rich phase, supporting studies can be conducted in order to use this non-distillable phase as an additive in the rubber industry or asphalt production.

## SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/11379>, or from the corresponding author on request.

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## ИЗВОД

УНАПРЕЂЕНО ДИЗЕЛ ГОРИВО ОД ПОБОЉШАНОГ ПИРОЛИТИЧКОГ УЉА  
ДОБИЈЕНОГ ПИРОЛИЗОМ ГУМА

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Пиролитичко уље (ТРО), добијено термичком пиролизом отпадних гума, није гориво еквивалентно дизелу које се може користити директно у возилима, због своје велике густине, вискозности и садржаја сумпора, ниске тачке паљења и ниског цетанског индекса. Поменуто уље се може користити само ограничено, мешањем са дизел горивом (DF), у количинама мањим од 30 %. У овој студији, пиролиза отпадних гума је спроведена при брзини загревања од 5 и 10 °C min<sup>-1</sup> у опсегу од 450 до 600 °C, коришћењем мешавине хијерархијског зеолита (HZSM-5), мезопорозног силицијум-диоксида (MCM-41) и живог креча (CaO) као катализатора. Добијени ТРО и каталитичко пиролитичко уље (CPO) су унапређени претходном обрадом, дестилацијом смеше напуњеног мезопорозног Cu(I) алуминосиликата (Cu(I)-MAS) и MCM-41, а затим корацима одсумпоравања и обезбојавања. Да би се добило гориво слично дизелу, побољшано каталитичко пиролитичко уље (UCPO) и биодизел (PBD) добијен од палминог уља су мешани у одре-

ђеним размерама. Густина, вискозитет, тачка паљења и цетански индекс добијених дизел горива су били у границама граничних вредности дизел горива.

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