

KAUNAS UNIVERSITY OF TECHNOLOGY

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**REPROCESSING THE RUBBER OF USED
TIRES INTO LIQUID FUELS**

Summary of Doctoral Dissertation
Technological Sciences, Chemical Engineering (05T)

2016, Kaunas

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SIMBOLIAI IR SANTRUMPOS

BR – Polybutadiene Rubber;

HCS - Hydrocarbons

IBP – Initial Boiling Point

IP – Induction Period;

ISI – Information Sciences Institute

MEA – Monoethanolamine;

SBR – Styrene–Butadiene Rubber;

T/O – *Tire/Oil*;

TGA – Thermogravimetric Analysis.

INTRODUCTION

Each year, the demand of a growing industry and the public for fuel promotes the more intensive searches of alternative energy sources. One of the possible alternatives for non-renewable energy sources are polymeric waste due to its high energy potential.

According to recent statistics, each year a worldwide accumulation of waste tires exceeds 20.2 million tons which complement the growing amount of non-biodegradable waste. Some of these tires are restored and returned to the market. When it is not possible to re-use such tires, they are usually disposed of in the landfills or incinerated in the industrial furnaces.

A more innovative handling of waste tires is their reprocessing into fuel since the calorific value of tires is very high and it depends on their elemental and chemical composition. Therefore, the products (gas, liquid, and char) obtained from tires have a high energetic value as well. One of the more attractive ways of reprocessing used tires into fuel is thermolysis. Depending on the fractional and chemical composition of the liquid thermolysis product obtained from scrap tires, the product can be used as multi-purpose fuel or as a component of fuel production.

Solid residue obtained after tire thermolysis (char) could be applied variously, for example, as a carbon black in the production of new tires or to be burned as fuel. Also, char could be upgraded to activated carbon, which has been successfully applied as an adsorbent for a wide spectrum of pollutants [phenols, mercury, pesticides, and chromium (VI) and as a support for metallic catalysts.

The aim of this work is to investigate the thermolysis process of used passenger car tires and determine the influence of process conditions on the yield, composition, physical, and chemical properties of the thermolysis products.

The objectives of the work are:

1. To investigate the influence of process pressure, tire shredding degree, and quantity of used engine oil on the yield of gaseous, liquid, and solid products;
2. To calculate the constants of chemical kinetics and state functions of thermodynamics of tire rubber and *Tire/Oil* mixture thermolysis using the data of thermogravimetric analysis;
3. To investigate the influence of process conditions and type of material on the component composition of liquid thermolysis product.
4. To analyse the physical and chemical properties of products;
5. To determine the optimal conditions of tire and *Tire/Oil* mixture thermolysis process which produce the highest yield of gasoline and diesel fuel;

6. To determine the efficiency of hydrogenation process for removing sulphur compounds from liquid thermolysis product.

Scientific novelty:

This research has investigated the influence of excessive pressure [40 and 80 bar (gauge)], the tire shredding degree under that pressure, and the quantity of engine oil in the *Tire/Oil* mixture on the yield and properties of the thermolysis generated products, as well as the fractionation and component composition of the liquid products.

Significance of research results

The present research has determined the optimal conditions for tire rubber and *Tire/Oil* mixtures thermolysis which produce the highest yield of liquid product. The research shows that a higher yield of naphtha and diesel is obtained from the thermolysis of *Tire/Oil* mixtures than from tires alone. The principal schemes of thermolysis of *Tire/Oil* blends and hydrogenation of naphtha and diesel fractions obtained from liquid thermolysis product are proposed.

The main statements of the defence:

1. A higher yield of naphtha and diesel is obtained from *Tire/Oil* mixtures thermolysis than from tires and the yield of the liquid product is more influenced by the shredding degree of tires and the quantity of engine oil than by the process pressure; the engine oil decreases the activation energy of the chemical decomposition process.
2. After desulfurization, the quality of the liquid product corresponds to the requirements for automotive fuel.

Scientific approbation of dissertation

The results of the doctoral dissertation work were presented at 3 scientific conferences, 2 of them international, and 2 articles were published in reviewed scientific journals listed in the Journal Citation Report (ISI).

1. EXPERIMENTAL SETUP AND METHODS

1.1. The Object of Research

In this research, the feedstock was waste summer and winter car tires, which were produced by five of the most popular automotive tire manufacturers: Continental, Michelin, Goodyear, Dunlop, and Pirelli. All brands of car tires were cut into three different fractions [50x50x10/15 mm (*1 type*; trapezoid shape); 50x25x10/15 mm (*2 type*; trapezoid shape) and 1x1x1 mm (*3 type*; cube shape)]. After that, the same brand and size tires were mixed in equal parts (0.5 kg of each) by mass and homogeneity in the mixer for 10 min, at the rotational speed 30 rpm.

During the process of thermolysis the shredded waste car tires were thermally decomposed plain or mixed with an appropriate amount of engine oil (Table 1.1).

Table 1.1 Composition of the *T/O* Mixtures

Solid feedstock	<i>T/O</i> mass ratio			
	<i>1 type</i>	2:0	2:1*	2:2
<i>2 type</i>	2:0	2:1	2:2	0:2

*Value of one part is 0.5 kg

For the mixtures, ultra-high quality synthetic oil Q8 T 860 SAE 10W40 was collected from the locomotive diesel engine at intervals of approximately 23,000 km. Before mixing, the oil samples were filtered through 100 μm pore filter. Before thermolysis, the oil sample and tire pieces were dried by heating at 110 °C for 24 h.

The thermolysis processes of shredded tires, *T/O* mixtures, and oil were conducted in 3000 cm³ capacity semi-continuous vertical reactor which was connected to a cooling and condensation system of the reaction products and the equipment for the separation of liquid and gaseous products (Figure 1.1).

In all thermolysis experiments, a hermetically sealed reactor, loaded with the appropriate amount of feedstock under nitrogen gas, was heated by an electrical muffle furnace raising the temperature from 20 to 550 °C at a heating rate of 2.5 °C/min. In the case of tires, the decomposition process was carried out at atmospheric, 40 bar, and 80 bar pressures, but in the case of the *T/O* mixtures and engine oil only atmospheric and 40 bar pressures were used. Throughout the process, independently of the mixture composition, the furnace was transferring heat to the reactor at a constant 3 kW power.

During the thermolysis processes, the gaseous and liquid products were separated in the separator. The thermolysis oil accumulated in a tank, and non-condensable thermolysis components flowed through the gas meter to the torch

or gas sample branch pipe. The solid-phase product remained in the reactor, which was discarded after the system cooled.

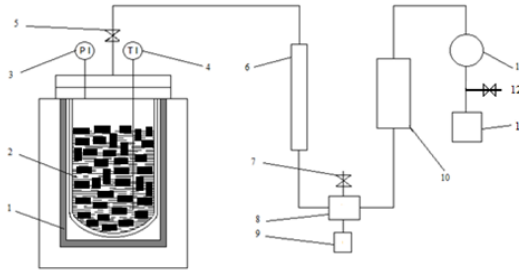


Figure 1.1 Schematic diagram of the *T/O* mixtures thermolysis unit: 1 – heating furnace, 2 – reactor, 3 – pressure transducer, 4 – thermocouple, 5 – valve, 6 – air condenser, 7 – safety valve, 8 – separator, 9 – liquid product tank, 10 – water reflux condenser, 11 – gas meter, 12 – gas sample branch pipe, 13 – torch.

During the thermolysis process, the pressure and temperature were recorded with the valve (Figure 1, position 5) open. For pressurized experiments, the valve was kept closed until the pressure in the reactor reached 40 or 80 bar (gauge). Afterward, the valve was opened, and vapour-phase products were released from the reactor for further processing. The process terminated when the gas ceased to flow from the reactor and the temperature in it reached 550 °C. The reprocessing time of *T/O* mixtures, intermediates, and the end products depended upon the chosen pressure; the whole build-up rate was affected by the thermochemical processes taking place in the reactor.

The methodology for calculations of the activation energy and thermodynamic parameters

The kinetics of tires, engine oil, and *T/O* mixtures decomposition reactions were calculated by ASTM E1641 standard and Flynn–Wall method. For such type of reactions, the reaction kinetics was studied using thermogravimetric data. It was considered that the change of conversion during the reaction was proportional to the reaction rate (formula 1.1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha); \quad (1.1)$$

Where: $k(T)$ is a temperature-dependant reaction rate constant, α – conversion, t – time, $f(\alpha)$ is a conversion function. The degree of conversion is usually estimated according to the formula (1.2):

$$\alpha = \frac{m_i - m_t}{m_i - m_f}; \quad (1.2)$$

Where: m_i , m_f and m_t are the initial, final, and current sample mass at the moment t , respectively. The reaction rate constant for the decomposition reaction is described by the Arrhenius equation (1.3):

$$k = A \exp\left(\frac{-E}{RT}\right); \quad (1.3)$$

Where: A is the pre-exponential factor, E is the apparent activation energy, T is the absolute temperature and R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Activation energies were also calculated by standard method ASTM E1641 using the following equation (1.4):

$$E = -\left(\frac{R}{b}\right) \Delta(\log\beta) / \Delta\left(\frac{1}{T}\right); \quad (1.4)$$

Where: E is the apparent activation energy, A is the pre-exponential factor, R is the gas constant, $\Delta(\log\beta)/\Delta(1/T)$ – slope, β – heating rate, T – absolute temperature, b – an integration derivative taken from standard ($b = 0.457$), a – value too from the standard; α – conversion, T_C – the temperature at a constant degree of conversion.

Activation energies can also be calculated using the Flynn–Wall equation: (1.5):

$$\log\beta = \log \frac{AE_a}{RG(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT}; \quad (1.5)$$

Where: b is the heating rate; A is the pre-exponential factor; E_a is the apparent activation energy; $G(a)$ is the mechanism function; R is the gas constant; and T is the Kelvin temperature.

The E_a can be calculated from the slope of $\log b$ vs $1/T$ for the given $G(a)$. The advantage of this method is that E_a is directly calculated without using the mechanism functions which would result in errors. In addition, the Flynn–Wall method can cover a wider range of degree of mass conversion and make no assumption about the order of reaction in calculation of activation energy. The pre-exponential factors (A) and other thermodynamic parameters, such as Enthalpies difference (ΔH), Gibbs free energies difference (ΔG), and entropies difference (ΔS), were calculated by Eqs. (1.6 – 1.9) (Kim-Yong, Kim-Young, & Kim, 2010):

$$A = \beta E_a \exp\left(\frac{E_a}{RT_m}\right) / (RT_m^2); \quad (1.6)$$

$$\Delta H = E_a - RT; \quad (1.7)$$

$$\Delta G = E_a + RT_m \ln\left(\frac{K_B T_m}{hA}\right); \quad (1.8)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (1.9)$$

Where: K_B is the Boltzmann constant, and h is the Plank constant. T_m is the peak temperature.

Hydrogenation of liquid thermolysis product

In this study, the hydrogenation treatment of the liquid thermolysis product from polyolefin and heterorganic compounds was performed with an ideal plug flow reactor (Figure 1.2.). The reactor (2) was loaded with CoMo sulphide on aluminosilicate catalyst and connected to the hydrogen recirculation systems, raw material feed pump, a high (6) and low (7) pressure separator, and two adsorption columns (12, 13) of the gaseous product cleaning. The raw feedstock was supplied to the reactor at 320 °C temperature, 0.4 mL/min flow (feedstock mass rate of 0.5 t/(m³·h), mixed with recirculated hydrogen gas in the ratio of 1:300, by volume (standard conditions). The process pressure was kept 51 bar. The conversion products from the reactor were drained to a high–pressure separator (6) where the majority of hydrogen and hydrogen sulphide were, and dried hydrocarbon gas (methane and ethane) was separated from it. The liquid fraction from the high pressure separator pumped to low pressure separator (7) where the liquid product was separated from the C₃ and C₄ gases. The gaseous products from both separators were removed through the upper part and the liquid products – through the bottom of the separators. The mixture of the gaseous products from the high pressure separator got in to the absorbers 12 and 13, where the gases were scrubbed of hydrogen sulphide. The purified gas mixture was diluted with fresh hydrogen gas so that the concentration of hydrogen gas in the recirculated flow would not be less than 90% and returned to the upper part of the reactor. Excess gas was burned in the torch.

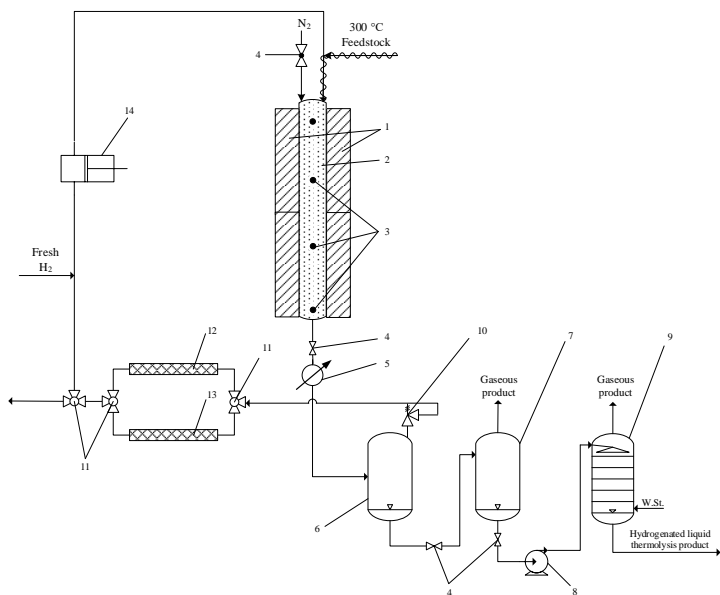


Figure 1.2 Principal scheme of catalytic hydrogenation of liquid thermolysis product: 1 – heating elements, 2 – reactor, 3 – thermocouple, 4 – valve, 5 – water cooler, 6 – high pressure separator, 7 – low pressure separator, 8 – pump, 9 – stabilization column, 10 – safety valve, 11 – 3-way valve, 12, 13 – adsorption columns, 14 – hydrogen pump

2. THE MAIN RESULTS AND DISCUSSION

2.1. The Influence of Thermolysis Process Parameters on the Yield of the Thermolysis Products

2.1.1. The Influence of the Tire Shredding Degree and Process Pressure on the Yield of the Thermolysis Products

The yield distribution of liquid, solid, and gaseous products obtained at the thermolysis process of waste tires under different pressures and shredding degrees of the feedstock are shown in Figure 2.1. As seen from the histogram, pressure in the reaction zone has a different effect on the yields of three aggregation state thermolysis products. It is observed that the feedstock size has a similar influence on the product yields, too.

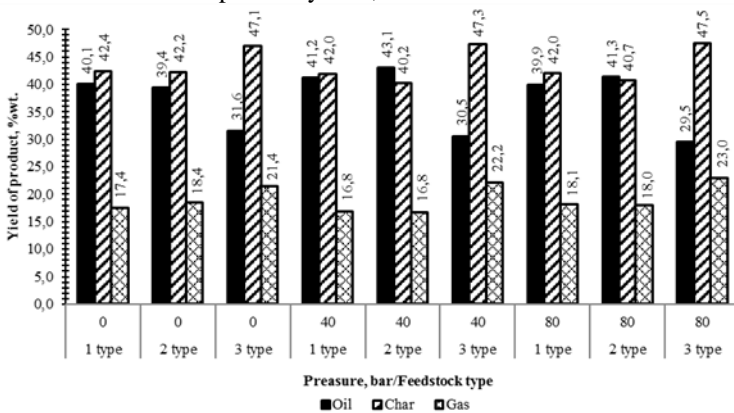


Figure 2.1 The yield distribution of thermolysis products by process pressure and the shredding degree of raw material.

The highest yield of the target product, i.e., the thermolysis oil, 43.1% (w/w), is obtained when 2 type feedstock is reprocessed at 40 bar pressure. The same feedstock processed at atmospheric pressure produces a 3.7% (w/w) lower yield of liquid product (Laresgoiti, et al., 2004); (Ucar, Karagoz, Yanik, Saglam, & Yuksel, 2005); (Berruero, Esperanza, Mastral, Ceamanos, & Garcia-Bacaicoa, 2005). The rest of the two types of feedstock processed at atmospheric and 40 bar pressure do not give distinct and unique liquid product yield differences. The feedstock shredding to the highest degree (3 type) has the greatest influence to the liquid product yield.

The pressure increase to 80 bar results in no significant increase (about 2%, w/w) in the liquid product yields, as expected; they appear even lower (by 1–2%, w/w) than at a process pressure of 40 bar. Thermolysis of 3 type feedstock

produces considerably lower yields (by 7.8–13.6%, w/w) of the liquid product at any process pressure.

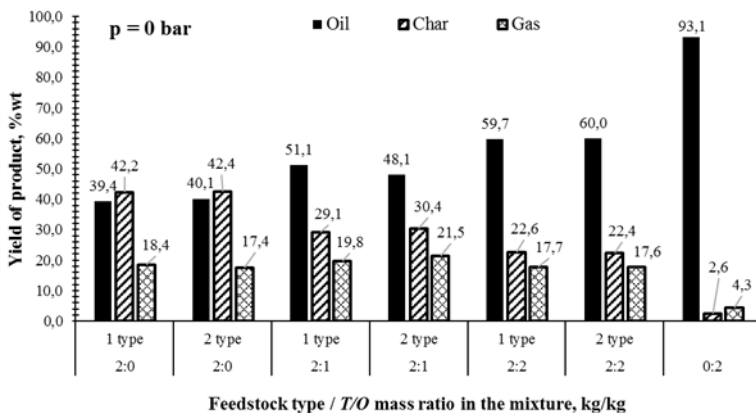
The highest yields of solid products are obtained when the thermolyzed feedstock is shredded to the finest particles, 3 type. In this case, however, the process pressure does not have significant influence on the fixed carbon yield.

2.1.2. The Influence of Composition of the T/O Mixture and Process Conditions on Yield of the Thermolysis Products

Figure 2.2 presents the yield distribution of gaseous, liquid (oil), and solid (fixed carbon) products which are obtained under different thermolysis process pressures, shredding degrees of tires, and T/O ratio. The results show that the oil additive in thermal decomposition processes of tires gives a larger amount of liquid product. On the other hand, these conditions require longer residence times of feedstock that allow the formation of more gaseous products. Processing tire rubber with half as much of used oil (2:1) generates about 1.4–7.8% (w/w) more gaseous products as compared to thermolysis of tires alone. However, in case of 2:2 mixtures the changes in gas yield are practically negligible. The yield varies in the range of 16.5 to 18% (w/w).

The oil additive in thermal decomposition reduces the yield of solid phase. The conversion processes (Figure 2.2) of 2:1 and 2:2 mixtures show that the yield of the solid phase decreases by 6.45–11.8% (w/w) and 14.3–17.4% (w/w), respectively, in comparison with the thermolysis of tires. The highest yield of liquid product derived from tire thermolysis is 43.1% (w/w), when the thermolysis process is carried out at a pressure of 40 bar and the size of tire specimen is 50x25x10/15 mm (2 type). When the T/O blends are used at the same conditions, the process pressure has the opposite effect on the yield of the

a)



b)

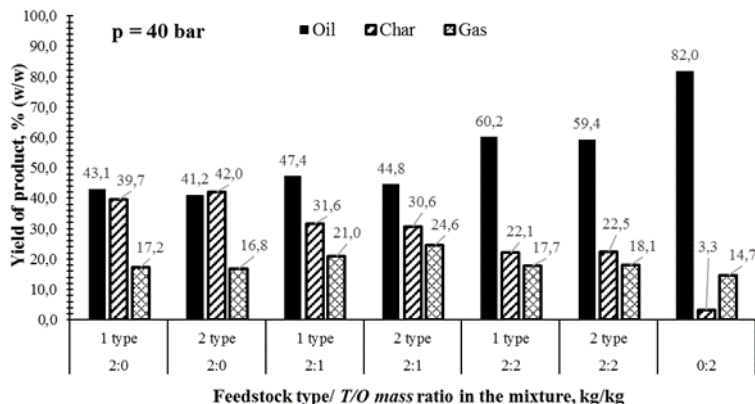


Figure 2.2. Yield distribution of thermolysis products in respect to the shredding degree of raw material and tire to oil ratio.

liquid product to tire thermolysis, i. e. when the *T/O* mixtures are processed in ratio of 2:1 at elevated pressure (40 bar) (Figure 2.2b) the yield of the liquid product reduces by 3.3–3.7% (w/w), compared to the corresponding results of atmospheric thermolysis.

The investigation of the influence of the feedstock particle size (*1 type* and *2 type*) in *T/O* mixtures on the yield of liquid thermolysis product reveals that reprocessing finer solid feedstock (*2 type*) produces more (up to 3%, w/w) liquid product at any process pressure.

Summarizing the results, the feedstock shredding degree and process pressure are important process parameters that affect the amount of target product derived from scrap tires. Thermolysis studies show that the optimal conditions of thermal destruction of tire in 3000 cm³ capacity semi-continuous vertical reactor which generate the maximum liquid product yield (43.1%) are 40 bar pressure and *2 type* material. In the case of *T/O* mixture thermolysis, the liquid product yield is more affected by the oil content of the mixture than by the tire shredding degree or process pressure.

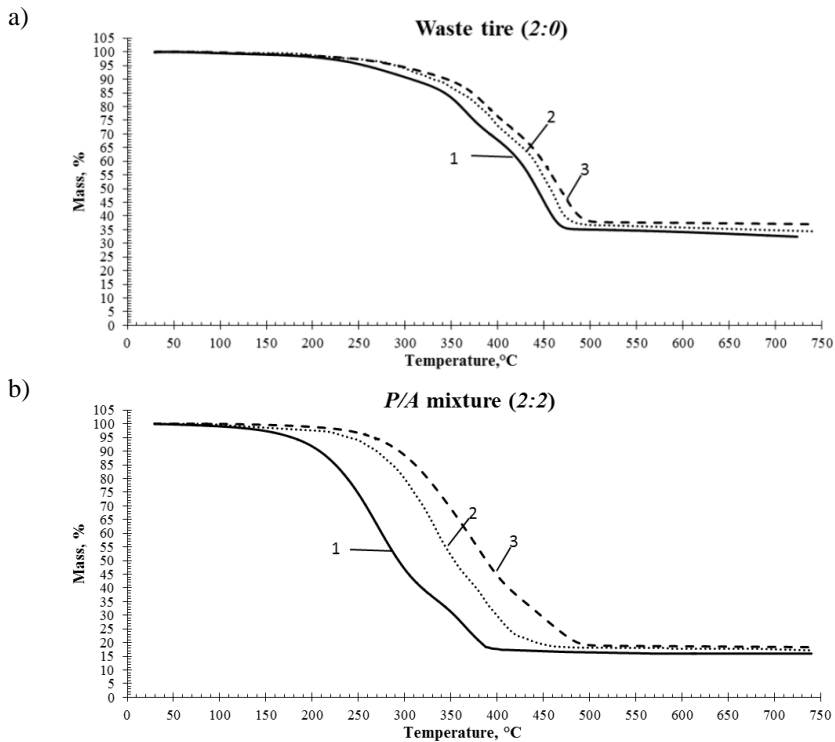
2.2. Kinetic and thermodynamic parameters of tire thermolysis

Thermolysis reactions of waste tires, used oil, and their mixtures occur by the mechanism of radicals. In case of the pure car tire decomposition (Figure 2.3a), the curves of thermogravimetric analysis (TGA) are more horizontal than others, i. e., engine oil and *T/O* mixture. The reason is that the tires are made of different kinds of materials, e.g. natural (cis-polyisoprene) and synthetic rubber (SBR and BR), various plasticizers, and other additives (Chen & Qian, 2003),

which have a sufficiently wide (200–490 °C) temperature range of disintegration. Moreover, the TGA curves show that the tire rubber decomposition is less complete than *T/O* mixture and generally consists of two steps, describing the temperature at which the material achieves a maximum decomposition speed. The first step (340–350 °C) indicates the decomposition of polyisoprene rubber (natural rubber); the second stage (340–350 °C) shows thermal decomposition of polybutadiene rubber (synthetic) (Onenc, Brebu, Vasile, & Yanik, 2012).

It is observed (Figure 2.3b) that the decomposition process of the *T/O* mixtures has two stages as well, but in contrast to tire decomposition, the maximums of these stages are at a lower temperature range. The peak of polyisoprene decomposition (the first step) is at about 225–230 °C and polybutadiene (the second step) – at about 350–360 °C.

The kinetic and thermodynamic parameters of feedstock for each degree of conversion (0.1; 0.5; 0.9) have been calculated according to ASTM E 1641 standard and Flynn–Wall methodologies. All calculations have been performed



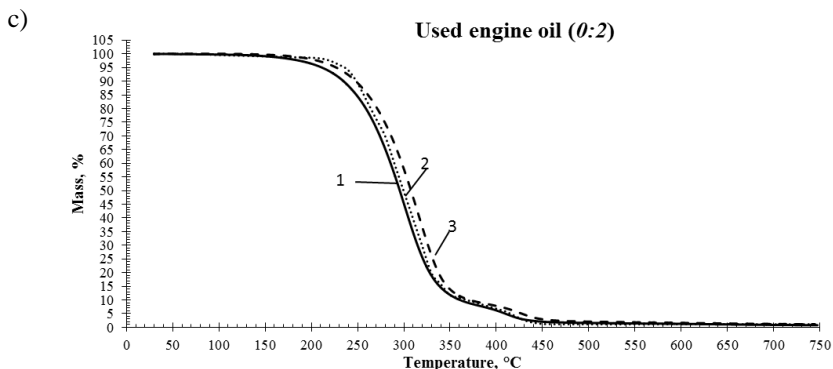


Figure 2.3 The TG curves of the waste tires, used oil, and *T/O* mixture (2:2), under different rates of thermal destruction: 1 – 2.5 °C/min, 2 – 5 °C/min and 3 – 10 °C/min.

at 2.5 °C/min temperature rising speed, which corresponds to the pilot experiment in the reactor. The results are given in Table 2.1.

Table 2.1 Kinetic and Thermodynamic Parameters of Thermolysis Process at Different Degrees of Feedstock Conversion 0.1; 0.5; 0.9.

Conversion, α	Temperature, T_{konv}	Pre-exponential factor, A	Activation energy, E_a	Entropy difference, ΔS	Enthalpy difference, ΔH	Gibbs energy difference, ΔG	Const. of reaction rate, k
–	K	–	kJ/mol	J/mol·K	kJ/mol	kJ/mol	–
<i>Waste tire</i>							
0.1	548.68	$8.86 \cdot 10^8$	104.30	–87.01	99.73	147.48	0.10
0.5	678.80	$1.40 \cdot 10^{17}$	233.42	68.16	227.77	181.51	0.15
0.9	733.72	$1.08 \cdot 10^{22}$	319.97	161.07	313.87	195.69	0.18
<i>T/O blend (2:2)</i>							
0.1	473.14	29.10	26.40	–229.04	22.46	130.83	$3.6 \cdot 10^{-2}$
0.5	550.38	59.20	34.16	–224.39	29.58	153.08	$3.4 \cdot 10^{-2}$
0.9	638.47	306.52	48.11	–211.96	42.80	178.13	$3.6 \cdot 10^{-2}$
<i>Used engine oil</i>							
0.1	507.76	$2.41 \cdot 10^{22}$	223.25	170.83	219.02	132.28	0.26
0.5	568.38	$3.04 \cdot 10^{27}$	304.99	267.55	300.27	148.20	0.28
0.9	629.23	$7.43 \cdot 10^{49}$	604.81	695.28	599.58	162.08	0.46

The data in Table 2.1 show that the highest activation energy (223.25 kJ/mol, conversion degree 0.1) is needed to decompose used engine oil. In the case of waste tires, it is approximately half as high (104 kJ/mol) as compared to used engine oil. However, the TG analysis reveals that using the mixtures of these two wastes the activation energy which is needed to split the molecules is greatly reduced to about 26.4 kJ/mol (conversion – 0.1).

The change of entropy values indicates (Table 2.1) that at the beginning <641.16 K (~368 °C temperature) of the tire thermolysis process the decomposition reactions are slow ($\Delta S^\ddagger < 0$) but as the temperature rises above this value, the reaction rate increases ($\Delta S^\ddagger > 0$). With reference to *T/O* mixtures, slow reactions prevail with a slight tendency of acceleration ($-229.04 < \Delta S^\ddagger < -211.96$ J/mol·K).

In all cases, the constant of reaction rate for different feedstocks is almost the same, i.e. 0.1–0.18 of waste tire, 0.26–0.34 of used engine oil, and $3.37 \cdot 10^{-2}$ – $3.65 \cdot 10^{-2}$ of *T/O* mixtures.

2.3 The Composition and Properties of Liquid Thermolysis Product

2.3.1. The Component Composition and Properties of the Liquid Thermolysis Product Derived from the Tire

The data of gas chromatography show that the thermolysis oil is a very complex mixture of all classes of hydrocarbons (Kaminsky & Mennerich, 2001). In the case of atmospheric thermolysis, major compounds in liquid-phase products are arenes (37–41%), alkenes (22–24%), alkanes (15–24%), and dienes (7–11%). The results (Table 2.2) show that when the process pressure increases to 40 bar, the amount of aromatic components and dienes decreases by 2–7% and 5–7%, respectively; the amount of alkenes increases by 1–5%, and the amount of alkanes increases by 6–15%. As the thermolysis pressure is doubled (80 bar), the saturated hydrocarbons become dominant in the product. The amount of alkanes found is nearly twice as high as in the oil produced from tire thermolysis under atmospheric pressure.

The analysis results of aromatic compounds of thermolysis oil are partly consistent with the results published by Kyari et al. (Kyari, Cunliffe, & Williams, 2005), who state that oil contains mainly alkylated benzenes and alkylated indenenes. The compounds that have been identified include benzene, toluene, ethylmethylbenzene, ethylbenzene, styrene, xylenes, naphthalene, and phenol. As it is seen from Table 2.2, the increase of pressure in the reactor decreases the amount of benzene by 2–5% and toluene by 1–2.5%.

Minute amounts (1.25–3.02%) of limonene, the formation of which in the tire thermolysis process is described by Laresgoiti et al. (Laresgoiti, et al.,

2004), have been observed in the liquid products obtained under atmospheric pressure thermolysis. As the pressure of the conversion process increases, only trace amounts of limonene are detected in the products.

Table 2.2 Amount of Compounds of Different Hydrocarbon Classes in Thermolysis Oil derived from tire

Property and organic compds class, %	<i>Feedstock type, Pressure and T/O mixture ratio</i>								
	0 bar; 1 type	0 bar; Type2	0 bar; 3 type	40 bar; 1 type	40 bar; Type2	40 bar; 3 type	80 bar; 1 type	80 bar; Type2	80 bar; 3 type
Heating value (MJ/kg)	41.98	42.12	41.75	42.27	42.04	42.42	42.24	42.08	42.56
Density, kg/m ³	903	902	908	898	893	890	900	901	885
Sulfur (wt %)	0.63	0.60	0.6	0.66	0.67	0.74	0.59	0.50	0.57
Water content (wt %)	3.98	3.9	3.59	4.23	4.47	6.83	4.60	3.23	6.41
Alkanes	15.53	22.23	23.51	30.49	28.13	31.43	40.57	39.10	39.23
Alkenes	23.39	22.35	23.92	26.23	26.83	24.85	17.62	16.28	16.40
Alkynes	0.22	0.24	0.31	0.33	0.31	0.10	0.18	0.30	0
Dienes	10.20	8.52	7.21	2.94	2.70	2.13	2.29	1.44	1.04
Trienes	1.47	0.65	1.49	0	0.13	0.53	0.13	0.07	0.37
Aromatic HCs	40.86	40.31	36.83	34.34	35.42	34.88	34.91	37.89	39.00
Benzene	11.75	11.79	10.53	7.71	6.87	8.62	7.68	8.40	8.09
Toluene	10.91	10.26	10.84	8.43	9.34	8.84	8.86	9.00	8.56
Furanes	0.95	1.00	1.00	0.94	1.12	1.61	1.01	1.13	2.40
Other	7.38	4.7	5.73	4.73	5.36	4.47	3.29	3.79	1.55
Total:	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The highest water content (6.83 and 6.41%, w/w) is detected when the 3 type feedstock is thermolyzed at 40 and 80 bar pressure; it is almost twice as high as the smallest values of the water content in the oil. Thus, the water content of the liquid product is more influenced by the particle size of the feedstock than by the process pressure.

2.3.2. The Component Composition and Properties of the Liquid Thermolysis Product Derived from the T/O Mixture

In contrast to tires, the liquid product obtained from pure oil is composed predominantly of alkanes (41%) and olefins (40%). The results in Table 2.3 show that the thermolysis process at elevated pressure generates less dienes and

trienes, whereas the yield of more stable alkanes increases with pressure and the quantity of waste oil in the *T/O* mixture. The highest yield of alkanes (38.66%) is gained when *I type* feedstock and engine oil are mixed in a ratio of 2:2 and reprocessed at 40 bar. A comparison of the quantities of saturated alkanes in the oil derived from thermolysis under elevated and atmospheric pressures reveals that the amount of these compounds increases by 9–15%. When pure waste engine oil is used, the content of saturated hydrocarbons in liquid product increases by almost 17% in comparison with the results obtained under atmospheric thermolysis.

The data of experiments at elevated pressure (40 bar) shows that the influence of pressure on the quantity of aromatic hydrocarbons derived from the *T/O* mixtures in a ratio of 2:1 and 2:2 was insignificant; the values fluctuate in the range of 1–2%. The quantity of other aromatic compounds (ethylmethylbenzene, ethylbenzene, xylenes, naphthalene, indane, and phenol) remains similar in the liquid product under different process conditions.

The liquid product obtained from tire thermolysis usually has the water phase alongside the organic phase. However, it should be noted that for the *T/O* mixtures under any thermolysis conditions and mixture compositions, water does not form in the liquid product; only trace amounts of water have been detected.

The sulphur content in the thermolysis oil derived from pure oil and tire under atmospheric pressure is 0.29% (w/w) and 0.58–0.66% (w/w), respectively. The processing of the *T/O* mixtures (2:2) results in increased sulphur content in the liquid product by 0.22–0.27% (w/w). When the thermolysis process is performed at elevated pressure (40 bar), the amount of oil in the *T/O* mixture has no influence on the sulphur content in the main product. In this case, the sulphur content resembles that of the liquid product from tires, i.e. 0.6–0.67% (w/w).

The liquid thermolysis oil derived from tires and *T/O* mixtures is characterized by high calorific value (41.5–42.5 MJ/kg from tire and 43–44.5 MJ/kg from *T/O* mixtures), low ash content (0.01–0.11%, w/w), and moderate sulphur content 0.5–0.74% (w/w). These properties make the product energetically valuable by itself or partly suitable for manufacturing liquid fuel for industrial and domestic furnaces, foundries, and boilers in power plants, or suitable for upgrade to a high-quality automotive fuel.

Table 2.3 Amounts of Compounds of Different Hydrocarbon Classes in Thermolysis Oil derived from *T/O* mixtures

Property and organic compds class, %	<i>Feedstock type, Pressure and T/O mixture ratio</i>									
	<i>1 type; 0 bar</i>		<i>1 type; 40 bar</i>		<i>2 type; 0 bar</i>		<i>2 type; 40 bar</i>		<i>Used Oil</i>	
	<i>2:1</i>	<i>2:2</i>	<i>2:1</i>	<i>2:2</i>	<i>2:1</i>	<i>2:2</i>	<i>2:1</i>	<i>2:2</i>	<i>0 bar</i>	<i>40 bar</i>
Heating value (MJ/kg)	44.4	43.0	43.9	44.5	42.9	42.8	43.8	44.0	45.6	46.1
Density, kg/m ³	851	823	840	836	871	846	848	813	816	810
Sulfur (wt %)	0.78	0.9	0.67	0.73	0.7	0.82	0.58	0.65	0.29	0.27
Water content (wt %)	0.24	0.6	0.03	0.14	0.03	0.03	0.04	0.17	0.02	–
Ash (wt %)	0.01	0.08	0.11	0.11	0.01	0.05	0.01	0.09	0.04	0.05
Alkanes	26.9 8	29.42	37.25	38.66	19.53	18.36	34.24	29.61	40.74	57.51
Alkenes	26.1 4	34.54	24.71	30.46	30.95	33.80	21.06	32.24	39.04	28.95
Alkynes	0.26	2.83	1.27	0.43	0.00	2.45	1.01	0.00	1.32	0.00
Dienes	3.70	1.93	1.98	1.84	7.50	6.16	1.97	1.37	5.26	2.49
Trienes	1.45	1.39	0.92	0.87	0.00	0.78	0.07	0.00	0.00	0.00
Alcohols	4.53	2.08	1.39	2.57	2.48	1.53	2.29	2.02	3.53	0.09
Aromatic HCs	29.9 6	23.45	31.56	21.84	34.40	28.33	34.48	29.80	5.91	8.55
Benzene	2.81	2.16	2.83	2.38	6.67	6.85	4.35	8.15	0.80	1.33
Toluene	4.65	4.16	5.80	4.43	10.17	8.56	5.66	9.52	1.94	2.92
Other	6.98	4.36	0.92	3.33	5.14	8.59	4.88	4.96	4.20	2.41
Total:	100	100	100	100	100	100	100	100	100	100

2.3.3. Investigating the Fractional Composition of the Liquid Product

The results of distillation of all liquid thermolysis products show that the initial boiling points (IBPs) of liquid products derived from tires lay in the narrower temperature range of 59–70 °C (Figure 2.4) while the IBPs of the liquid products obtained from *T/O* mixtures and engine oil are in the 42–84°C range (Figure 2.5). The highest content of naphtha compounds in two tire liquid products derived from *3 type* feedstock under pressure of 40 and 80 bar (boiled to 200 °C) is 58.9% and 51.2% (v/v), respectively. The rest of the liquid thermolysis products are less rich and contain naphtha fractions in the range of

32–39% (v/v). These liquid products are also rich with the diesel fraction and are suitable as feedstock for the production of diesel and related fuels.

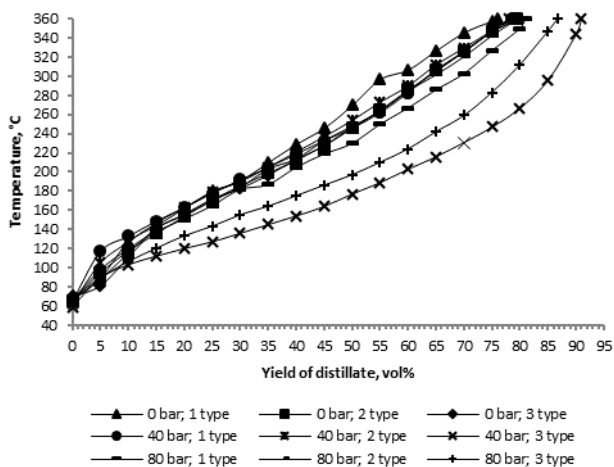


Figure 2.4 Distillation characteristics of thermolysis liquid products obtained from tire

The distillation curves show that the main parameter which affects the amount of naphtha and diesel fractions in the liquid products obtained under pressurized thermolysis is the shredding degree of the raw material rather than the pressure in the reactor.

The yield of the naphtha fraction in the thermolysis oil obtained from *T/O* mixtures is in the range of 12–48% (v/v). More compounds fall into the diesel fraction that boils in the temperature range of 200–360 °C. The yield of this fraction varies from 36% to 52% (v/v) and depends on the composition of primary components and the process conditions. The minimum yield of the diesel fraction (36%, v/v) is obtained when the pure oil thermolysis is carried out under atmospheric pressure. The yield of naphtha and diesel fraction is influenced not only by the relative composition of the *T/O* mixture but also by the size of shredded tire specimen. In *T/O* mixtures prepared from *2 type* feedstock and engine oil mixed in a ratio of 2:2, the yield of naphtha decreases almost by half in comparison with the yield of naphtha derived from the mixture in a ratio of 2:1. When these two types of mixtures are thermolyzed at elevated pressure (40 bar), the yields of naphtha and diesel fraction increase by 5.4% (v/v) and 1.3% (v/v), respectively.

The yield distribution of these two fractions with regards to *1 type* feedstock is heavily influenced by the process pressure.

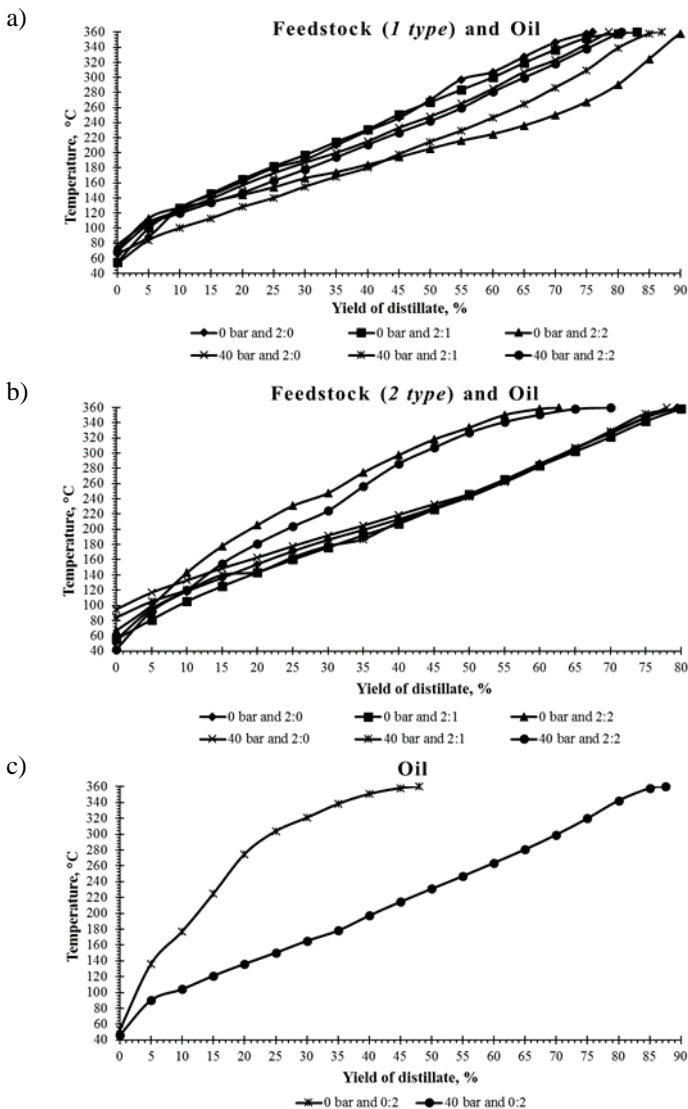


Figure 2.5 The distillation characteristics of thermolysis liquid products obtained from *T/O* mixtures and used engine oil

2.4. Cleaning the liquid thermolysis product by hydrogenation

During the thermolysis process, the sulphur compounds from the feedstock are transferred into the liquid product (0.31–0.86% from tire, 0.27–0.29% from

engine oil, and 0.58–0.9% from *T/O* mixtures); however, they are undesirable in fuel due to the negative impact on the environment, people, and the motor. Catalytic hydrogenation is a way to remove these undesirable compounds from the liquid thermolysis products.

As the experimental data show (Table 2.4), the most effective purging of sulphur compounds is achieved using the CoMo/ γ -Al₂O₃ catalyst, 300 °C

Table 2.4 The Influence of Catalytic Hydrogenation Parameters for Desulphurization of Raw Feedstock

Feedstock	Feedstock flow rate, ml/min	Temperature, °C	Sulphur content, mg/kg	Yield of product, %
Liquid product of tires	0.4	300	9.6	97.3
	0.5		58.9	98.1
	0.6		78.4	97.8
Liquid product of <i>T/O</i> mixtures	0.4	300	8.3	96.8
	0.5		31.5	97.6
	0.6		67.3	97.4

temperature, and 0.4 ml/min feedstock feed rate to the reactor. This way, the sulphur content in the liquid product reduces from 7400–9000 mg/kg to 8.3–9.6 mg/kg. Besides, the unpleasant smell is removed and dark brown (black) color of the product is changed to orange (in the case of tires) and lime green (in the case of *T/O* mixtures) using the hydrogenation cleaning with CoMo/ γ -Al₂O₃ catalyst.

The results of chemical composition (Table 2.5) show that catalytic

Table 2.5 The Influence of Catalytic Hydrogenation Parameters for Desulphurization of Raw Feedstock

Property	From tire		From <i>T/O</i> mixture	
	Before Hydrogenation	After Hydrogenation	Before Hydrogenation	After Hydrogenation
Heating value (MJ/kg)	41.98	42.15	44.41	44.79
Sulfur (mg/kg)	0.74	0.0096	0.90	0.0083
Density 20 °C (kg/m ³)	903	893	851	812
Kinematic viscosity 40 °C, mm ² /s	3.3218	3.1721	2.9281	2.7536
IBP (°C)	66	100	55	104
Water content (% , w/w)	0.03	0.09	0.24	0.35
Ash (% , w/w)	0.02	0.04	0.01	0.03
Coke (% , w/w)	9.18	5.47	1.44	0.90
Saturated HCs (% , w/w)	13.28	43.74	42.6	90.98
Unsaturated HCs (% , w/w)	17.92	3.64	44.65	0.69
Aromatic HCs (% , w/w)	55.89	51.9	4.28	3.83

hydrogenation has a significant effect on the chemical composition. The quantity of unsaturated hydrocarbons decreases from 17.92–44.65% to 0.69–3.64%, while

the quantity of saturated hydrocarbons increases from 13.28% to 43.74% in the liquid product obtained from tires and from 42.6% to 90.98% in product obtained from *T/O* mixtures. Catalytic hydrogenation also has an effect on the chemical stability; it confirms the results of oxidative stability (Figure 2.6).

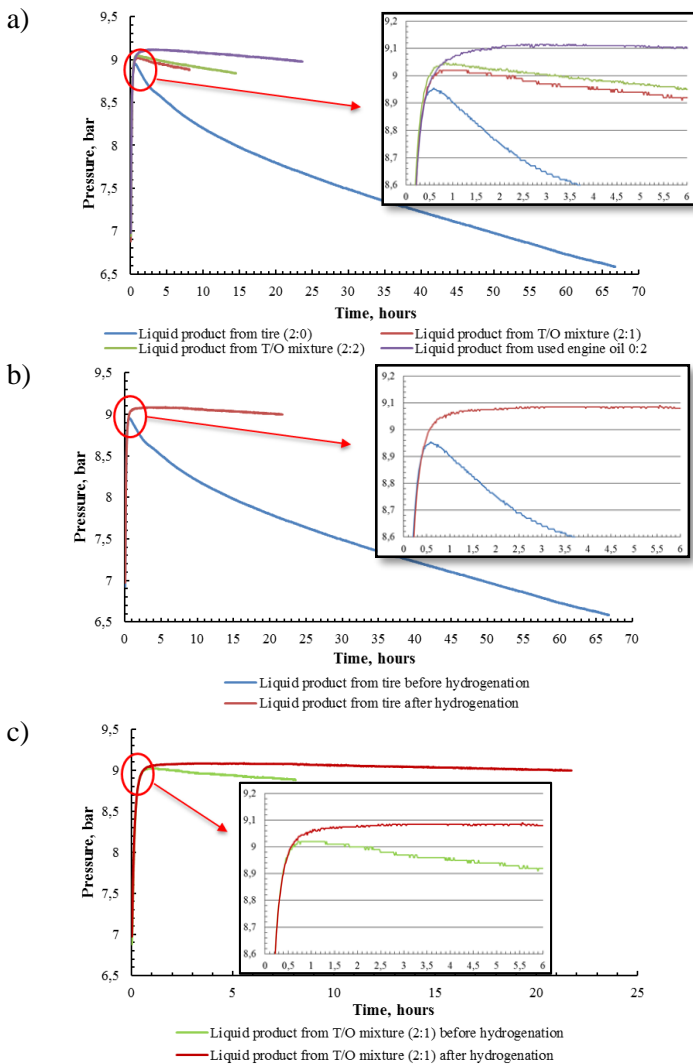


Figure 2.6 Curves showing the oxidative stability of the liquid thermolysis product: a – before hydrogenation, b, c – after hydrogenation

The results in Figure 2.6a show that the liquid product derived from tires has the lowest oxidative stability (induction period (IP) is only 0.98 hours) compared to the other products. However, after the hydrogenation process (Figure 2.6b and 2.6c) the chemical stability of tire liquid product increases from 0.98 to 3.04 hours. Using the liquid products obtained from *T/O* mixtures the IP increment is much higher, i.e. from 2.11 to 20.1 hours.

2.5 Technological recommendations for tire and *T/O* mixtures thermolysis process and hydrogenation of liquid thermolysis products

The chosen conditions of car tire and *T/O* mixture thermolysis allowed producing the highest amount of naphtha and diesel from 1 ton of feedstock (Table 2.6 and 2.7).

Table 2.6 The process conditions of tire thermolysis producing the highest yield of naphtha and diesel

Tire			
Fraction	Feedstock type	Pressure, bar	Yield, kg
Naphtha	3 type	40	179.6
Diesel	2 type	40	192.7

Table 2.7 The process conditions of *T/O* mixture thermolysis producing the highest yield of naphtha and diesel

<i>T/O</i> mixtures				
Fraction	Feedstock type	<i>T/O</i> ratio, kg/kg	Pressure, bar	Yield, kg
Naphtha	1 type	2:2	0	288.0
Diesel	2 type	2:2	40	276.9

The thermal decomposition process of tire and *T/O* mixtures consists of the following stages: loading the reactor with raw materials (shredded car tires with/without used engine oil), shutting the loading/unloading port, removing air from the system and filling it with nitrogen gas, raising the temperature from 25 to 550 °C, cooling the reactor to 100 °C, opening the loading/unloading port, and unloading the solid product. A work cycle is composed of all these stages. The duration of one work cycle is 12 hours, so one reactor can execute 730 work cycles per year. For one cycle, 100 kg of shredded tires and 100 kg of used engine oil are necessary.

The recommended principal technological scheme for tire and *T/O* mixture thermolysis is presented in Figure 2.7. Appropriate amounts (100 kg of each) of shredded tires and used engine oil from tanks (T-1 and T-2) are processed in 0.3475 m³ capacity semi-continuous vertical reactor (R-1/5). The thermolysis system consists of five identical reactors, which are involved in the process one after another, every 3 hours. The operating temperature of the reactors is from 25

to 550 °C, pressure 0–40 bar, and the working time is 6 hours. Before the start, the air is removed from each reactor with a vacuum pump (VS–1). and the system is filled with nitrogen gas. In the thermolysis process, the reactors are heated (for about 2.5 hours) with process gas derived from the reactor which performs the thermolysis, until a sufficient volume of gas product forms in the heated reactor. The heating rate of each reactor is regulated with automatic temperature indicator controller (TIC 1/5) which controls the gas flow into the combustion chamber via valves (V–16/20).

To reduce heat loss, the combustion products flowing out of the combustion chamber are used to heat the reactor before the start, as well as the cyclone (CS–1) and heat exchanger (TK–1). The pressure in the reactor is controlled by the pressure indicator controller (PIC 1/5) connected to the valves (V–1/4/7/10/13).

After the thermolysis process, the reactor is cooled with the fan (O–1) blowing the air into the heating chamber. When the temperature of the reactor reaches 100 °C, the loading/unloading port (marked by red colour) is opened and the solid product is removed by vacuum from the reactor to the tank (T–3).

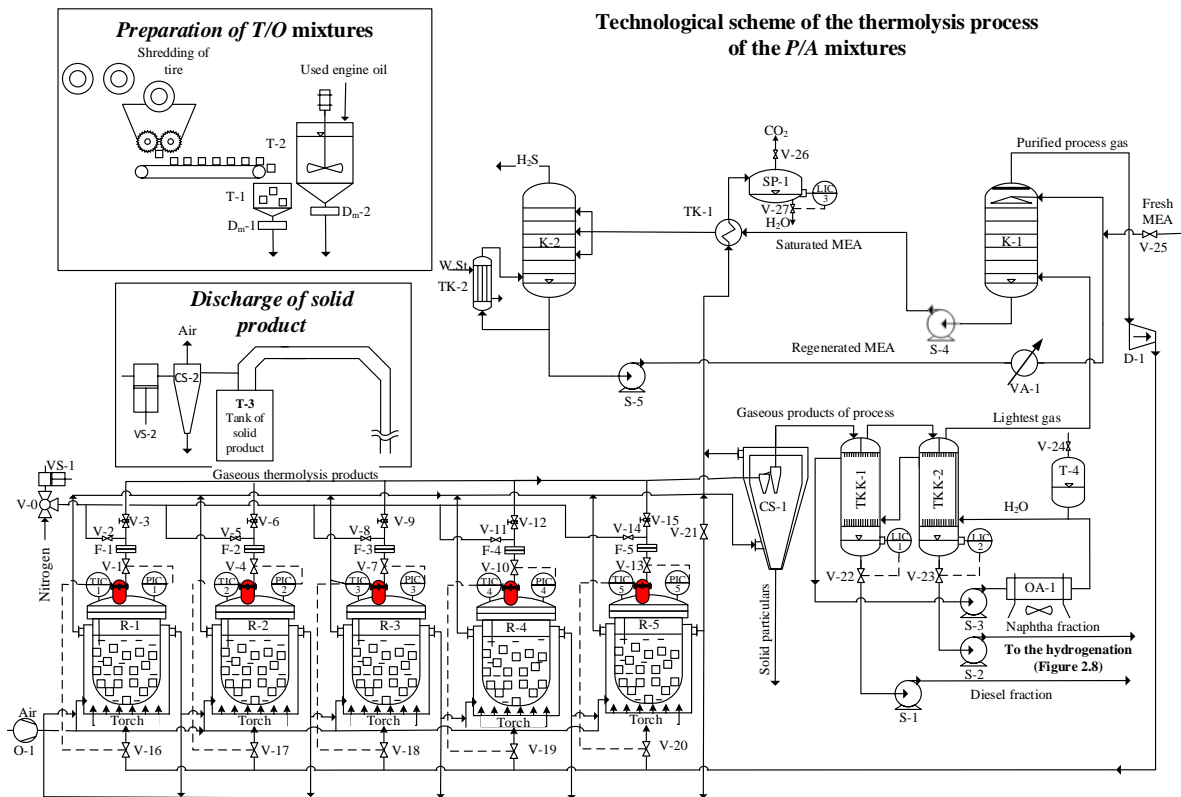


Figure 2.7 Principal scheme of tire and T/O mixtures thermolysis

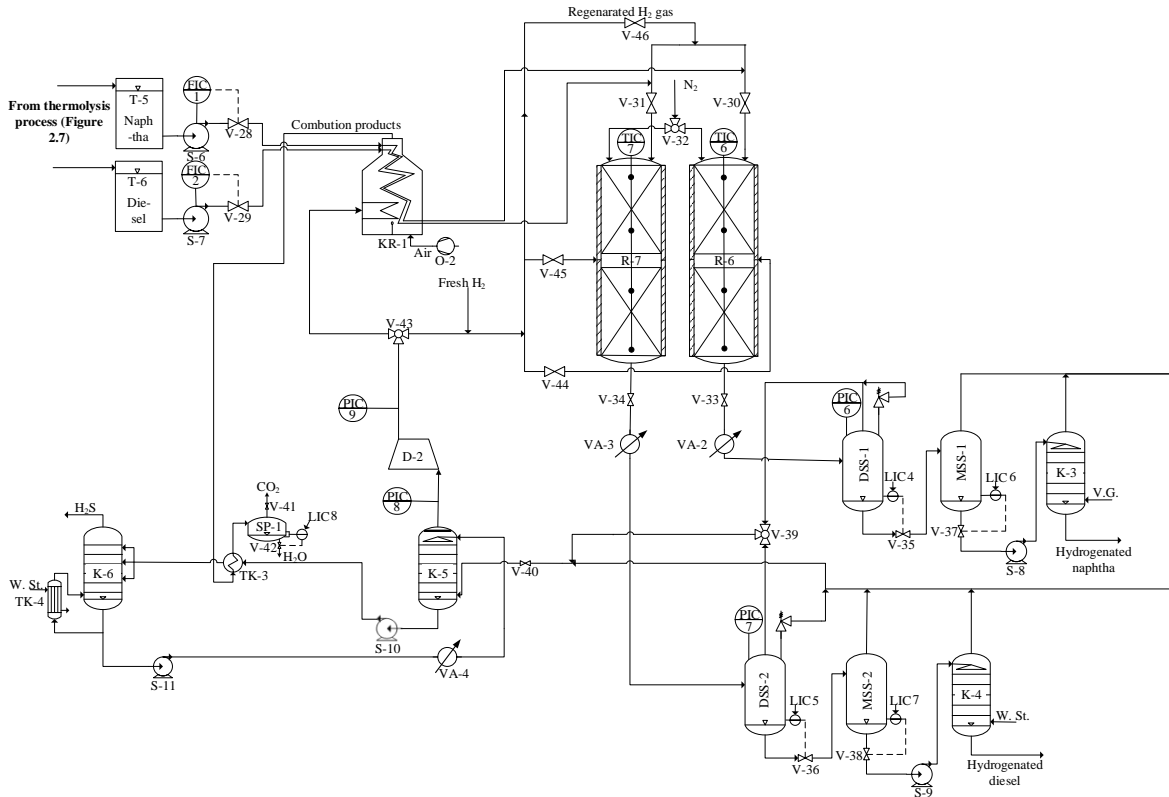


Figure 2.8 Principal scheme of naphtha and diesel hydrogenation

Firstly, the gaseous products obtained from the *T/O* mixture thermolysis process are cleaned from the solid particles in the cascade of cyclones (CS-1). Then they get into the condenser (TKK-1), where the diesel fraction (>200 °C) is separated; finally, the naphtha fraction is separated in the condenser (TKK-2). Naphtha and diesel fractions from the condensers are transported to the hydrogenation device (Figure 2.8). The remaining lightest hydrocarbons (thermolysis gas) from the condenser (TKK-2) get into the absorption column (K-1), where the sulphur compounds are removed using monoethanolamine (MEA) solution. Sulphur-free gas is transported to the torch of the reactor's combustion chamber.

The hydrogen sulphide separated from the MEA solution in the desorption column (K-2) is used for the production of elemental sulphur or pressed into balloons.

The hydrogenation process of the naphtha and diesel fractions derived from the liquid thermolysis product is presented in Figure 2.8. Using the centrifugal pumps (S-6 and S-7), naphtha and diesel fractions from the tanks (T-5 and T-6) are transported to the heating furnace, where the temperature of these fractions increases to 300–320 °C. Before the hydrogenation process the hot fractions are mixed with hydrogen gas in the ratio of 1:500, by volume. The flow of the fraction and hydrogen mixture to the reactor is controlled by flow indicator controllers (FIC 1 and FIC 2) connected to valves (V-28 and V-29). The retention time of the mixture in the reactor is 30 seconds.

The conversion products drained from the reactor are cooled with water coolers (VA-2 and VA-3) and transferred to high pressure separators (DSS-1 and DSS-2), followed by low pressure separators (MSS-1 and MSS-2). The separated liquid phases are transported to the stabilization columns (K-3 and K-4), where hydrogen sulphide is removed using the water steams (120 °C). All gaseous products from the separators and stabilization columns transmit to the column (K-5) where the gaseous products are desulphurised using MEA solution.

CONCLUSIONS

1. It has been determined that the yield of liquid product derived from used car tires increases (43.1%) with pressure up to 40 bar, except when the smallest fraction of tire (*3 type*) is used. Increasing the pressure to 80 bar decreases the yield of target product by about 1–2% but increases the solid (to 0.6%) and gaseous (to 1.3%) phases. Meanwhile, when the amount of engine oil in the *Tire/Oil* mixture increases to 2:2, the yield of the liquid product increases at the same pressure and is not affected by the growing process pressure.
2. The kinetic and thermodynamic calculations supported by thermogravimetric analysis has reveal that in the beginning (~368 °C temperature) of the tire thermolysis process the decomposition reactions are slow ($\Delta S^\ddagger < 0$), but when the temperature rises above this value, the reaction rate increases ($\Delta S^\ddagger > 0$). In the case of *Tire/Oil* mixtures only slow reactions prevail with a small tendency of acceleration ($-229.04 < \Delta S^\ddagger < -211.96$ J/mol·K).
3. The chemical composition of liquid products obtained from tires and *Tire/Oil* mixtures under atmospheric pressure shows that the products are predominantly composed of aromatic hydrocarbons. The quantity of alkanes in the liquid product increases with higher process pressure and tire shredding degree. However, the increasing of process pressure decreases the yield of alkenes, alkynes, dienes, trienes, and aromatic hydrocarbons in the liquid phase.
4. The liquid products derived from tire and *Tire/Oil* mixtures thermolysis have low ash (0.02–0.11%) and sulphur content (0.5–0.9%). The liquid products obtained from tires have lower calorific value (41.0–42.5 MJ/kg) and higher density (885–908 kg/m³) than the liquid products derived from *T/O* mixtures (43–46 MJ/kg and 813–871 kg/m³).
5. The highest yield of naphtha (28.8%) and diesel (27.6%) is obtained from the *T/O* mixtures under the following reprocessing conditions: 0 bar, *1 type*, ratio 2:2 in the case of naphtha and 40 bar, *2 type*, ratio 2:2 in the case of diesel.
6. Catalytic hydrogenation of the liquid product under CoMo/ γ -Al₂O₃ catalyst, 0.4 ml/min feedstock flow rate, and 300 °C temperature of process, reduces the quantity of sulphur compounds in it from 7400–9000 mg/kg to 8.3–9.6 mg/kg.

REFERENCES

1. BERRUECO, C., ESPERANZA, E., MASTRAL, F., CEAMANOS, J., and GARCIA-BACAICOA, P. Pyrolysis of waste tyres in an atmospheric static-bed batch reactor: Analysis of the gases obtained. *Journal of Analytical and Applied Pyrolysis*. 2005, 74, 245–253.
2. CHEN, F., and QIAN, J. Studies of the thermal degradation of waste rubber. *Waste Management*. 2003, 23, 463–467.
3. KAMINSKY, W., and MENNERICH, C. Pyrolysis of synthetic tire rubber in a fluidised-bed reactor to yield 1,3-butadiene, styrene and carbon black. *Journal of Analytical and Applied Pyrolysis*. 2001, 58–59, 803–811.
4. KIM-YONG, S., KIM-YOUNG, S., and KIM, S. H. Investigation of thermodynamic parameters in the thermal decomposition of plastic waste-waste lube oil compounds. *Environmental Science & Technology*. 2010, 44, 5313–5317.
5. LARESGOITI, M., CABALLERO, B., MARCO, I. D., TORRES, A., TORRES, M., and CHOMÓN, M. Characterization of the liquid products obtained in tyre pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 2004, 71, 917–934.
6. ONENC, S., BREBU, M., VASILE, C., and YANIK, J. Copyrolysis of scrap tires with oily wastes. *Journal of Analytical and Applied Pyrolysis*. 2012, 94, 184–189.
7. UCAR, S., KARAGOZ, S., YANIK, J., SAGLAM, M., and YUKSEL, M. Copyrolysis of scrap tires with waste lubricant oil. *Fuel Processing Technology*. 2005, 87, 53–58.

LIST OF PUBLICATIONS

Articles in journals from Thomson Reuters “Web of Knowledge” list:

1. JONUSAS, A.; MIKNIUS, L. Effect of Pressure and Feedstock State on the Yield and Properties of Waste Tires Thermolysis Products // *Energy and Fuels*. 2014, 28, 2465–2471.
2. JONUSAS, A.; MIKNIUS, L. Influence of the Process Conditions on Yield, Composition and Properties of the Products Derived from the Thermolysis of Scrap Tire and Used Engine Oil Blends // *Energy and Fuels*. 2015, vol. 29 (11), 6978–6987.

Publications at international conferences

1. JONUSAS, A.; MIKNIUS, L. Influence of process conditions of tire thermolysis on composition of liquid product // 19th International scientific conference, university of Latvia, 2014 October 8-10./Riga, Latvia, 2014. ISSN 1691-4112. p. 31-32.
2. JONUSAS, A.; MIKNIUS, L. Reprocessing of waste tires into liquid fuel // Проблемы недропользования: International Forum – Competition of Young Researchers, National Mineral Resources University, 24th – 26th of April 2013/ St. Petersburg, 2013. ISSN 978–5–94211–646–0. p. 150–153. (Verbal presentation)

Papers in national conferences

1. JONUSAS, A.; MIKNIUS. Analysis of Liquid Product of Tyre Thermolysis // *Organinė chemija: mokslinės konferencijos pranešimų medžiaga = Organic chemistry: proceedings of scientific conference / Kaunas University of Technology*. Kaunas: Technologija. ISSN 2029–6401. 2012, p. 74–75.

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REZIUMĖ

Pagrindinis šio darbo tikslas yra padangų termolizės proceso tyrimas, siekiant įvertinti pasirinktų parametrų (padangų susmulkinimo laipsnio, slėgio ir variklinės alyvos priedo *Tyre/Oil (Padanga/Alyva)* mišinyje) įtaką termolizės produktų išeigai, sudėčiai ir fizikinėms bei cheminėms savybėms. Remiantis gautais tyrimų rezultatais buvo siekiama nustatyti optimalias darbinės sąlygas, kurių pagrindu būtų galima sukurti naujus technologinius sprendimus leidžiančius iš padangų ar jų mišinių su alyva gauti didžiausias benzino ir dyzelino frakcijų išeigas.

Tyrimams buvo panaudotas laboratorinis termolizės įrenginys, iširtos žaliavų ir termolizės metu susidarantių (dujinių, kietųjų ir skystųjų) produktų cheminė sudėtis, esant skirtingoms sąlygoms. Nustatyta, kad optimalios sąlygos leidžiančios gauti didžiausią benzino frakcijos išeigą (28.8 %) yra atmosferinis slėgis ir *Tipas 1* žaliava, kuri sumaišyta su naudota varikline alyva santykiu 2:2. O dyzelino (27.6%) atveju, slėgis reaktoriuje turi būti 40 bar bei naudojama *Tipas 2* žaliava, kuri taip pat sumaišyta su alyva santykiu 2:2.

Kadangi į skystąjį produktą termolizės metu pereina tam tikra dalis sieros junginių, kurie yra nepageidautini kure, buvo atliktas šių junginių šalinimas panaudojant hidrinimo procesą. Tyrimų metu buvo nustatytos optimalios sąlygos, kurioms esant likutinis sieros junginių kiekis yra žemiau leistinos ribos, t. y. <10 mg/kg.

Gautų tyrimų rezultatai palyginami su kitų autorių rezultatais gautais termolizuojant padangas ar jų mišinius su alyvomis bei šalinant sieros junginius.

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