

POSSIBLE USAGE OF PRODUCT FROM THERMAL CRACKING OF PROTECTED VULCANIZATES

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ABSTRACT

Waste tire utilization demands working out environmentally safe technologies affording valuable goods. One of the possible solutions is thermal cracking of waste tire. Thermal solution of waste rubber in high boiling oil products affords pitch –and asphalt-like materials. These products may be used (without being separated, by analogy with bitumens) in road building or as anticorrosive, waterproofing and other materials. The process will be much less expensive if the stages of solvent isolation and product separation are excluded.

The present paper studied the thermal cracking process of waste tire and considered the usage of dark oil product so called pyrolysis oil as an additional quantity of oil product.

Key words: *waste tire, thermal cracking, oil*

INTRODUCTION

In recent years, approximately 15 million tonnes of post consumer plastic waste is generated throughout Europe each year, while in the United State 20 million tonnes of waste is generated [3]. In general, plastic waste has been mainly disposed of by landfill or incineration, but these processes are not fully acceptable under current international policy, which focuses on efficient recovery of raw material and energy. Pyrolysis and gasification processes are promising routes for optimal upgrading from waste. Moreover, pyrolysis of plastic mixture, based on the decomposition of polymers at different temperatures, allows the treatment of polymers with simultaneous decomposition and separation [10,15]. These processes allow the obtainment of combustible, gases and/or energy, with the reduction of land filling as an added advantage [2]. The first step for a suitable design of any pyrolysis reactor is knowledge of the kinetics.

Thermogravimetric analysis (TGA) is widely considered as a useful technique to study solid decomposition processes, including their kinetic. The information that can be obtained from this technique can be useful for the design of reactor where the thermal decomposition of the solid takes place [8,9]. The mechanism of thermal degradation of waste plastic is very complex and includes, amongst others, the following reactions: chain fission, radical recombination, carbon–hydrogen bond fission, hydrogen abstraction, mild-chain β -scission, radical addition, etc. [11,12].

In some cases, sources of waste may generate a single type of plastic waste, but in the majority of cases, the plastic will be a mixture of types. Obviously, this fact implies an additional complication, and for this motive there are many studies on the pyrolysis of individual single types of plastic, simple plastic mixtures, mixed-plastic waste, and also copyrolysis of wood biomass and synthetic polymer mixtures [1,3–5,10,15].

Waste management is an important issue in both developed and developing countries nowadays [1,2,9,10,15]. Organic wastes, such as used rubber [8,12] and plastic [11,13,15] are among the waste materials that represent problematic wastes on one hand and valuable potential as secondary raw materials on the other hand. To alleviate part of our energy crisis and environmental degradation, it has become imperative to make use of appropriate technologies for recovery of resources from non-conventional sources like organic waste. As the general trend is to limit landfill sites, the disposal alternatives left for organic waste will be incineration and recycling. Incineration may utilize the energy content of organic waste but is associated with the generation of SO₂, NO_x and other hazardous emissions. The problems that occurred in the earlier recycling technologies based on pyrolysis and gasification are such as low gas productivity and the wide spectrum of products. These problems are difficult to overcome due to only limited control of the product

composition in pyrolysis and gasification processes. Thermal plasma technology has been under active development for a long time [3]. The technology is now well established in metallurgical processing, materials synthesis etc. [4–6]. The extremely high temperatures generated by plasma torches have spurred development of their application to waste processing, as they are capable of significantly decreasing the waste volume to a non-leachable residue. By far the most important application of thermal plasma waste treatment is focused on the destruction of hazardous wastes [7,16] rather than recycling because of economic issues. Nevertheless, in recent years, the interest in energy and resource recovery from waste has grown significantly, and substantial research about the use of plasmas in organic waste treatment has been conducted. A review of the progress is presented in this paper. Because the progress of plasma pyrolysis technology is heavily dependent upon the availability of appropriate plasma generating devices, a brief discussion is also included on this topic.

Attempts to improve polymer–asphalt compatibility through addition of oils [1] or chemical modification of the asphalt binder have been reported in the literature [10].

Mixtures containing different types of polyolefins become softer in the presence of 5–30 wt.% oils in asphalt [1]. On the other hand, there are two types of residual pyrolytic oils, H09 and H18, available from the vacuum pyrolysis process of used tires. H09 is the heaviest cut of the vacuum pyrolysis process, which contains a high level of carbon black (10%) while H18 oil contains 1.8%. The process generates pyrolytic carbon black which can be totally separated from the pyrolysis oil. This pyrolytic carbon black is already used to modify asphalt [15]. Ciochina [2] and Chaala et al. [9] used both H09 and H18 along with some other pyrolytic oils to modify asphalt. They found that, depending on the type of asphalt, adding up to 10% of H18 to asphalt results in a decrease of the Fraass point of the mixture due to the very low Fraass point of H18. However, they reported that for concentrations higher than 10%, the resulting mixture possesses a higher Fraass point. Asphalt mixtures containing 5–10% of H18 are expected to result in materials with enhanced overall properties [8].

MATERIAL AND METHODS

All reagents used for the experiments were commercially available and were not purified further.

The raw material used was produced by Manufactory for rubber products in town of Yambol.

The process of thermal cracking was performed by methods described in [15]. The physico-chemical characteristics on the obtained liquid product are given in Table 1.

Tab. 1: Physical – chemical properties of pyrolysis oil.

Parameters	Methods	Values
Density at 20 °C	BSS EN ISO 3675:2004	0.8720
Sulphur, %	BSS EN ISO 8754:2004	0.19
Specific heat /lower/, kJ/kg	BSS EN ISO 1285:2003	40.45
Kinematic viscosity at 50 °C, mm ² /s	BSS EN ISO 3104:2001	4.45
Ash content, % (m/m)	BSS EN ISO 6245:2004	0.10
Water soluble acids and base	BSS 5252:1984	Neal
Flash point, °C	BSS EN ISO 2592:2004	105
Freezing point, °C	BSS 1751:1970	- 14
Water content, °C	BSS EN ISO 3733:2003	Neal

The present data have shown that pyrolysis oil, which is obtained in laboratory required of ecological norms of BSS for blend fuel oils, from one hand and from another it presented an excellent combustion parameters.

We investigated a conventional fuel oil produced from Bulgarian refinery by corresponding parameters to be made a comparison with a new alternative dark fuel, too. The second raw-material is commercial fuel oil which is required to BSS and EU norms. The obtained results are given in Table 2.

Tab. 2: Physical – chemical properties of conventional fuel oil.

Parameters	Methods	Values
Density at 20 °C	BSS EN ISO 3675:2004	0.9826
Sulphur, %	BSS EN ISO 8754:2004	0.88
Specific heat /lower/, kJ/kg	BSS EN ISO 1285:2003	43.20
Kinematic viscosity at 50 °C, mm ² /s	BSS EN ISO 3104:2001	7.45
Ash content, % (m/m)	BSS EN ISO 6245:2004	0.12
Water soluble acids and base	BSS 5252:1984	Neal
Flash point, °C	BSS EN ISO 2592:2004	115
Freezing point, °C	BSS 1751:1970	- 5
Water content, °C	BSS EN ISO 3733:2003	Neal

As can see from data presented in Table 1, obtained pyrolysis oil show good fuel characteristics but it has too many coke residue and ash content. Beside this it must notice that the obtained product required for sulphur content for dark fuel, but if it used in turbines it has too low kinematics viscosity. We decided to investigate the possibility to purifying this product trough adsorption by these and other ecological and economic reasons.

We use two adsorbents: commercial zeolite NaA and synthetic product Zeolite Z3 which was prepared by method of hydrothermal synthesis of granules from Bulgarian kaolin as main starting material. The conditions for thermal treatment of kaolin and hydrothermal crystallization (zeolitization) of granules are described in [5].

In Table 3 is given data about compositions of the initial mixtures for granulation.

Table 3. Compositions of the initial mixtures for granulation [5,6]

Components	Compositions, % (m/m)				
	Z ₁	Z ₂	Z ₃	Z ₄	Z ₅
1. Metakaolin	68.5	65.5	55.5	49.9	42.5
2. Carboxymethylcellulose	2.54	2.5	2.5	2.5	2.5
3. Zeolite Na A	15.0	15.0	20.0	20.0	25.0
4. 2 % solution of sodium hydroxide	10.0	12.0	15.0	18.0	20.0
5. 1.5 % solution polyvinyl alcohol	4.0	7.0	7.0	10.0	10.0

We studied adsorption process for purifying of raw material – pyrolysis oil with corresponding adsorbents. The method of adsorption equipment and conditions of the process were described in [11]. After purifying processes the obtained product was investigated by physical-chemical analyses. The obtained results are given in Table 4.

Table 4. Physical-chemical characteristics of pyrolysis oil obtained from thermal cracking

Parameters	Methods	Value	
		Z3	NaA
1. Kinematic viscosity at 40 °C, mm ² /s	BSS EN ISO 3104 + AC	2.25	2.23
2. Flash point, °C	BSS EN ISO 2719	59	61
3. Coke residue, % (m/m)	BSS EN ISO 10370	1.7	1.3
4. Ash content, % (m/m)	BSS EN ISO 6245	0.14	0.14
5. Sulphur content	BSS EN ISO 8754	0.60	0.60
6. Density at 15 °C	BSS EN ISO 3675	868.3	867.7
7. Distillation characteristic, (v/v)	BSS EN ISO 3405		
i.p, °C		42	41
200 °C		33.0	33.5
250 °C		54.0	54.5
300 °C		67.0	68.0
350 °C		79.5	81.0
e.p, °C		> 377	>375
8. Water content, % (v/v)	BSS 15862	neal	neal
9. Color	ASTM D 1500	2.0	2.0
10. Specific heat, kJ/kg	ASTM D 2500	39.55	39.45

As can see from the obtained results and experimental data from analyses after adsorption treatment the obtained products are much lighter, with better ecological characteristics and better distillation compositions.

It may concluded that purifying of pirolysis oil which is obtained by different methods from waste tires, polymers and protected vulcanizates is perspective way to obtain additional quantity fuel with appropriate ecological properties.

CONCLUSIONS

1. It's established that thermal processes of utilization of waste protected vulcanizates are processes with economical and ecological meaning.
2. It was shown the possibility for purifying of pirolysis oil by adsorption. As adsorbents are used commercial zeolite NaA and synthetic zeolite Z₃. The obtained data and results show that the obtained products may use as additional quantity of ecological dark fuel.
3. The method for purification of pyrolysis oil by adsorption is applied for the first time in RBulgaria.

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