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ACCOUNTING CHEMISTRY OF THE PROCESS WHEN SELECTING THE TEMPERATURE REGIME IN THE PYROLYSIS UNIT

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Abstract. *Thermal decomposition of the polymeric hydrocarbons, including rubber and other kinds of plastics is examined. Thermal decomposition – pyrolysis of heavy polymeric compounds has a great contrast to the thermal degradation of light hydrocarbon compounds based on general laws. The temperature regime of the pyrolysis unit based on general laws is selected for further testing in the laboratory model. Pyrolysis unit, which will be practiced temperature and process technology of pyrolysis of hydrocarbon polymers, including rubber and plastics was developed as a first approximation.*

Keywords: *thermal decomposition, pyrolysis, pyrolysis unit, recycling rubber and plastics, ecology*

Thermal decomposition of the polymeric hydrocarbon compounds is uneven in time and occurs at different temperatures. All polymers have high molecular weight varying from 1000 to 10 000, from 10 000 to 500 000 and more. The polymers molecular weight affects rheological characteristics of their melts (fluidity), thermal deformation behavior and a number of running abilities.

The macromolecules formed as a result of polymer reactions may be situated in the form of long molecular chains or form a grid. Monomers form a grid structure, in case they possess more than two reactive finite groups. Noncross-linked plastics are called thermoplastics. The thermoplastics can be composed either of linear or of branched molecular chains.

One of the most effective methods of plastics waste recycling is pyrolysis, which is the thermal destruction in the absence of oxygen during all process phases. The proposed method doesn't provide any emissions into the atmosphere. The pyrolysis regime is determined in every specific case depending on the waste composition.

As a result of the pyrolysis process, complex organic structure compounds composing polymeric materials are converted into simpler non-toxic liquid, oily and gaseous decomposition products. The blend composition consisting of paraffin, olefinic, cyclic, aromatic and heterocyclic hydrocarbons series can be further processed (condensation, capture, distillation, rectification, etc.) in order to obtain marketable products.

The polymeric hydrocarbon compounds don't have melting temperature; they firstly soften and then gradually melt from the periphery to the center. The melting time takes tens of minutes. As a result of long melting time and uneven heating during the pyrolysis process, apart from destruction some other high-temperature processes take place. The longer destruction products are in the high-temperature zone, the more poly-

condensation and polymerization products will be obtained, which also means more polycyclic aromatics and coke.

Along with the composition of raw materials, the quality of gaseous, liquid and solid process products will determine the softening, melting, destruction and sublimation time of decomposition products.

The temperature will determine the speed of the process depending on the raw materials. One can theoretically choose the temperature of polymer waste recycling in case of available raw materials and objective of getting the final product.

Table 1. The features and polymeric materials destruction products

Polymer	Melting temperature, °C	Destruction temperature, °C	Features and destruction products
Polypropylene	165-175	200-300	Carbon-carbonic bonds are fragile, as every second carbon atom in its main chain is tertiary and its hydrogen has excess reactivity.
Polystyrene	150	500-800	Destruction products are volatile compounds like monomeric styrene, its dimer and trimer. The main destruction products are ethane and benzene, the monomer amount is small - no more than 1 %.
Polyethylene terephthalate	250-280	> 800	Typical composition of the thermal destruction gaseous products (%): CO – 8.0; CO ₂ – 8.7; H ₂ O – 0.8; CH ₃ CHO – 80.0; C ₂ H ₂ – 2.0; other – 1.2.
Polyvinyl-chloride (PVC)	120-150	>> 160 200-250 > 400	Decomposition begins. The volatile products yield is 100 %. Thermal instability stands for dehydrochlorination process (C/c detachment with HCl release). The main chain is destroyed. Alkanes, alkenes, alkadiens and aromatics appear in destruction products.
Polyamide	205	>> 250	Water, carbon dioxide and a small amount of ammonia are isolated while destruction process.
Polyethylene	129-135	> 300	Liquid, oily and gaseous decomposition products are formed, but not ethylene.

Table 2. The pyrolysis of tires yield and combustion heat

Products, combustion heat	Pyrolysis temperature indexes, °C			
	500	600	700	800
Product yield (% of mass concentration):				
- solid	60.5	56.3	52.0	44.0
- liquid	30.3	29.1	27.9	17.7
- gaseous	6.8	12.5	18.2	26.2
- loss	2.4	2.1	1.9	2.1
Energy consumption MJ/kg	4.2	5.0	5.7	4.6
Combustion heat, MJ/kg:				
- Gaseous	34.018	39.040	44.095	37.768
- Liquid	44.125	43.125	42.080	25.620
- Solid	35.35	34.310	33.390	31.*080

Table 3. The calorific value and specific gravity of purified gas components.

Component	Specific gravity, kg/m ³	Calorific value, kcal/m ³
Hydrogen, H ₂	0.09	2590
Methane, CH ₄	0.717	8560
Hydrocarbons of ethylene series, C _n H _m	1290	1700
Carbon monoxide, CO	1250	3040

Analyzing the data of the Tables 1 and 2 we can draw the following conclusions. During this amount of polymeric hydrocarbons recycling one should specify the temperature range from 500 °C to 900 °C. Using this temperature range one can obtain the yield of gaseous, liquid and solid products by means of degradation. Gas corresponds to hydrocarbon gases (mainly CH₄ and some amount of CO, N₂, and O₂). Liquid phase corresponds to fuel oil-like liquid with molecular weight from 700 to 400. Solid product is soot, coke, reinforcement elements and mineral impurities.

Temperature rise will lead to greater gaseous products yield; when the temperature approaches the upper point of the interval 900 °C, not only C-C bonds, but C-H bonds will be destructed. This will lead to the hydrogen amount increase in the gaseous product. The destruction of thermostable alkanes such as ethane, methane begins at temperatures 600 °C, lower alkenes and cycloparaffins begin to decay at 700 °C. The destruction mechanism at temperatures higher than 700 °C includes the splitting of C-C and C-H bonds. With further temperature rise the decay rate increases and reaches a considerable value at 900 °C.

Along with the destruction, temperature rises from the 500 °C to the 900 °C, and the polycondensation reactions take place. The aromatic hydrocarbons, especially polycyclic ones, will be subjected to the reaction of dehydrogenation condensation with the asphaltene and coke formation. The gaseous and solids pyrolysis components rise occurs at the expense of the liquid phase.

The temperature drop to lower temperature range, that is to 500 - 600 °C will lead to destruction rate reduction, the gas volume decrease and the liquid component rise. The choice of pyrolysis temperature 600 °C, is based on the low temperature degradation of polymer compounds, including vulcanized rubber 400 - 500 °C (Table 2), the high output of the products obtained gaseous and liquid form ($12.5 + 29.1 = 41.6$) and low coke formation in the apparatus. The gas will correspond to limited and unsaturated hydrocarbon gases with small hydrogen volume and some amount of CO, N₂ and O₂. The liquid component of the decomposition products will correspond to wax-like product with molecular weight about 700. The product is subjected to distillation is difficult due to thermolability and high boiling point and can only be used in the process of carbonization. Coking products contain significant amounts of sulfur compounds. Kerosene and gasoil fractions will be components of fuel oil with sulfur content of about 3,0 - 3,5 % as part of the sulfides destroyed when exposed to heat and remove the light ends, most of the sulfur compounds left in the coke. Gasoline obtained coking is sent to the pyrolysis unit to increase the yield of pyrolysis gas.

Modern technology allows using the compact sets of adsorption (molecular sieves) identify products that are a valuable raw material for chemical production. This can occur after increasing the volume of pyrolysis plant, where economic realities will move fuel to natural gas, and pyrolysis gas clean split and sent for chemical production.

The most valuable components of the marketable output in the hydrocarbon polymer compounds pyrolysis are: styrene, isoprene, acetone, naphthalene, carbazole, benzene, toluene, gums. Purification and leading of these products to the salable condition is technically difficult on the one hand and expensive on the other. That's why some authors suggest building hydrocarbon polymeric compounds thermal decomposition production close to by-product coke plant to have the opportunity of gas purification facilities.

After condensation and capture of the monomeric chemical compounds and fractions residual gas contains 59 % of hydrogen, 26 % of methane, up to 7 % of carbon oxide, 3 % of ethylene series hydrocarbons and corresponds to high-calorific environmental friendly energy resource.

In the first stage we set ourselves the task to obtain high-calorific fuels in the gaseous, liquid and solid phases after polymeric compounds destruction with minimal products post-treatment.

In order to perform this task the pyrolysis process should be conducted within 500 - 600 °C temperatures during minimum length of time with possible elimination of coke and soot formation in the pyrolysis unit. This can be achieved in the case of the ground polymer materials hit into the moderate temperatures zone (to the 300 °C) of the unit, where it is heated, melted and then it gradually descends into higher temperatures zone. In the zone with 400 °C temperature the hydrocarbon polymers melting ends, and destruction and decomposition products evaporation begins. Other polymers keep melting, and the whole blend falls into the zone with 500 °C temperatures.

All plastics and vulcanized rubber intense destruction zone. The decomposition products boil and evaporate. Vapor phase rises up passing through the melt and the bulk material. The decomposition products heat the bulk material, and they are partially condensed, then they are cooled down to 300 - 350 °C and removed from the unit. The more refractory and high-boiling products fall into the zone with 600 °C temperature, where their melting, evaporation, destruction and then output in the gaseous and vapor phase out of the unit take place. At a given temperature 95 - 98 % of rubber melts and evaporates leaving the solid residue in the form of coke, metal cord, tires mineral impurities in the lower zone.

Outgoing from the unit products should be cooled, partially condensed and with 250 - 300 °C temperature sent to rectification and stabilization by dividing the products into three fractions. The gas component C₁-C₄ is used as fuel for the pyrolysis and coking processes. The liquid product is divided into gasoline fraction with initial boiling point – 200 °C, gas oil fraction with initial boiling point – 350 °C and heavy pyrolysis residue. The heavy product is sent without cooling through tight coupling to coke cube. The gas oil fraction is fuel oil component. The amount of sulfur in gas oil fractions of pyrolysis can be controlled by waste tires and plastics. The content of aromatic hydrocarbons in the light fractions (Table 5), is 2.38 % for raw materials, and benzene, and even less 0.54 %. Isolation of benzene from light fractions may be at high-volume processing. The gasoline fraction is sent to the pyrolysis unit under an inclined lower plate in the hydrocarbon polymers melting and decomposition zone with 550 - 600 °C temperature. The gasoline fraction is subjected to re-pyrolysis creating a hot upstream in the apparatus.

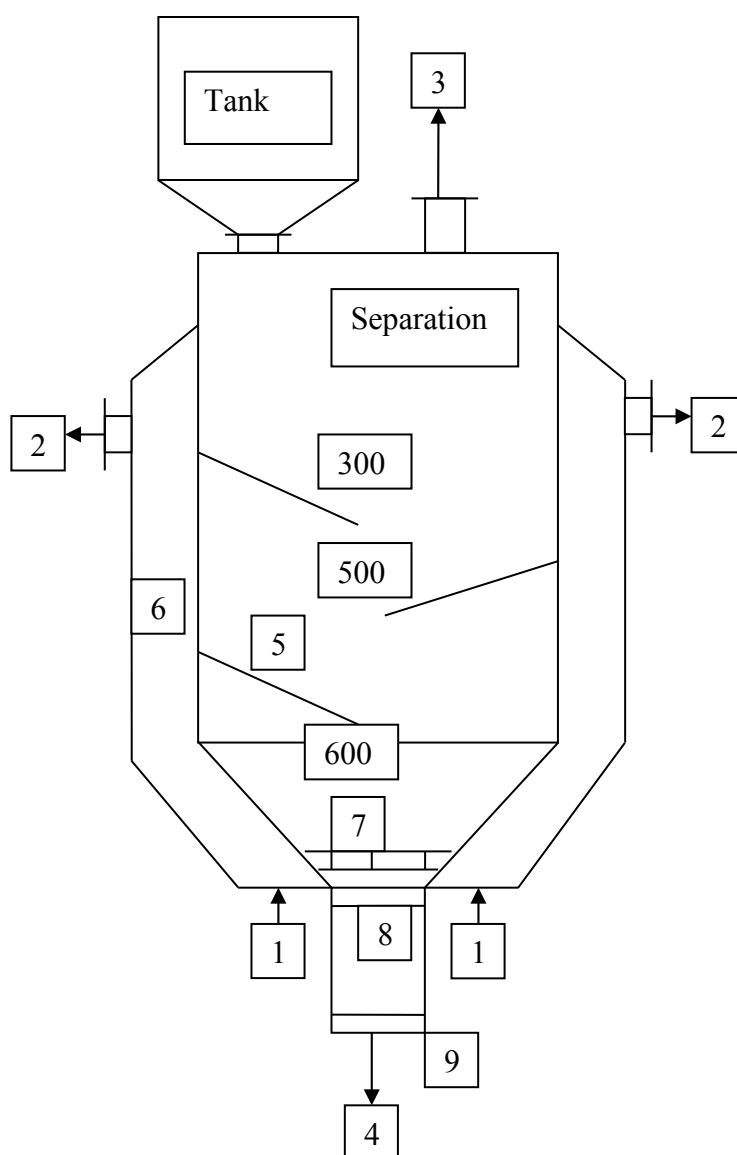


Figure 1. The rubber and plastics thermal decomposition unit:

- 1 – gas supply to the injectors; 2 – combustion gases outlet from a jacket;
 3 – cracking gases outlet; 4 – metal cord and coke discharge;
 5 – inclined perforated/sieve plates; 6 – unit jacket; 7 – furnace bars;
 8 – the upper gate valve; 9 – the lower gate valve.

Thermal decomposition zones:

- separation zone;
- 300 °C – heating zone;
- 500 °C – melting and destruction zone;
- 600 °C – monomeric compounds evaporation zone;
- solid products disposal zone

Table 4. BNR thermal decomposition under vacuum.
 (BN-rubber contains 70% of butadiene, 30 % of acrylonitrile.
 [With 400 °C temperature, vacuum residual pressure is
 1,0 mm Hg, yield - 95,0 % volatile, time 30 min])

Name of raw materials and products	Molecular weight M_{CP}	Yield, % of weight
Taken: 1. Butadiene rubber - BNR		100
Obtained: 1. Pyr. fr.	712	84,8,0
2. 25 °C fr.	63,7	15,2
3. 190 °C fr.	18	traces

Table 5. Product composition

Components	% Mol.
ethylene– C ₂ H ₄	9,1
ethane C ₂ H ₆	4,7 (13,8)
propadiene C ₃ H ₄	3,0
propylene C ₃ H ₆	2,9 (5,9)
butadiene C ₄ H ₆	14,1
butene C ₄ H ₈	8,3
butane C ₄ H ₁₀	3,3 (25,7)
cyclopentene C ₅ H ₆	2,5
Pentadiene C ₅ H ₈	9,1
Pentene C ₅ H ₁₀	4,8
Pentane C ₅ H ₁₂	1,6 (18,0)
benzene C ₆ H ₆	4,3
hexanediene C ₆ H ₈	6,6
hexene C ₆ H ₁₀	5,4
hexane C ₆ H ₁₂	2,7 (19,0)
from C ₇ to C ₁₀	17,6
Total	100

Note: Average molecular weight from six determinations was equal to 739

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