

Prospects for development of hydrocarbon raw materials resources reproduction

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Abstract: The article presents data on the influence of factors in the field of innovative technology of thermocatalytic depolymerization of solid household wastes (SHW) on the efficiency and prospects for the development of technogenic hydrocarbon raw materials resource reproduction. Process thermodynamics, reactions kinetics, the mechanism of thermolysis of secondary polymers in organic solvents have been studied by means of laboratory experiments. It is shown that different morphological groups of wastes dissolve practically at the same rate at temperatures of 250-310°C. A homogeneous product is formed in the liquid phase; the spread of values for the elements lies in the interval of 1.5-4.5 %; technological requirements of the stages of formation of boiler fuels are satisfied. Using the principles of patent analysis, new techniques of processing household waste components are proposed. The basics of energy-efficient and energy-saving processes of technogenic hydrocarbon raw materials resource reproduction have been laid. The possibility of increasing the production payback and intensification is shown. Ecological and demographic safety for population and technical and economic benefits from SHW processing are achieved.

1. Introduction

An innovative technology belongs to the priority area of state development: "Rational and safe nature management". It is necessary to apply biosphere-compatible recycling of solid household wastes, which are continuously reproduced by the population and pollute the surface of the lithosphere with polymers, which practically do not break down in nature; they exclude the deficit carbon from the biospheric and economic circulation. Annual accumulation of wastes in Russia is approaching 1 billion tons. Wastes removal and burial cause astronomical losses in the country. Deaths among population and absorption of the people's living space take place.

SHW is a primary geological formation. Current costs for preparatory and operational mining works are required.

It is necessary to reduce the cost of these unprofitable operations by achieving resource-productive utility [1, 2]. Academician K. N. Trubetskoy and Professor A. E. Vorobyev proposed to carry out a rapid (within a day) transformation of any organics into protopetroleum and gas raw materials on clays in the depths of the lithosphere for technogenic resource reproduction of hydrocarbon raw materials [1]. The company [2] suggests installing a plant for tires thermolysis under pressure into highly liquid petroleum derivatives.

In our technique, which is developed mainly in the patent environment via the Internet, hydrocarbon resource reproduction is carried out through the processes of SHW depolymerization [3, 4]. The objective of this work is to achieve environmental and demographic security for the population and payback of petroleum products, which are used for internal production purposes.

2. Materials and methods

Kinetics, thermodynamics and mechanism of polymers dissociation have been studied insufficiently. Well-known researchers studied the transformation of only selective substances.

The experimental data have been discussed in the reports of the Council of the Russian Academy of Sciences and Southwest State University.



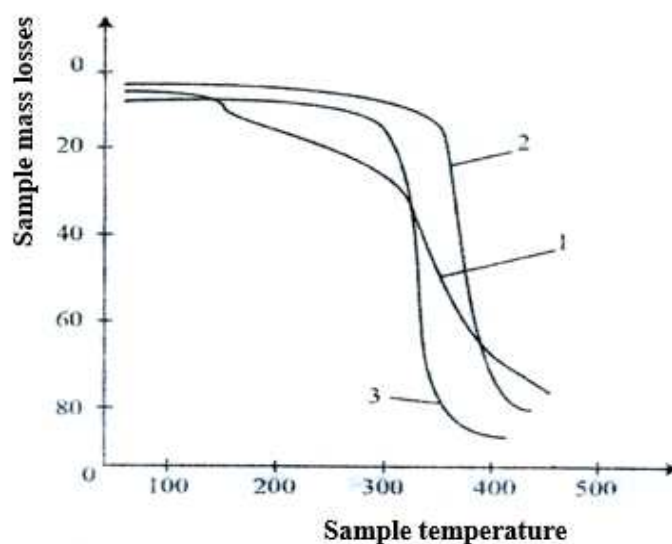


Figure 1. Polymers thermocatalysis depending on the temperature and composition of components: 1 - polymer composite material (umbrella polyethylene- and polyethylene terephthalate-based fabric); 2 - polyethylene terephthalate; 3 - polyamide

It is seen that a rapid jump in the polymer composition weight loss occurs above 200° C; mass loss reaches ~ 20 % at temperatures around 300° C. Rapid weight losses of all secondary polymer samples are already observed at temperatures above 350° C. The process of polymers depolymerization proceeds intensively, terminates and becomes irreversible at temperatures of 450-500° C.

The theoretical background of the new technology has been evaluated by means of experimental studying the chemical kinetics of the processes. The apparatus AKOV-10 was used. Heating of the heat-resistant flask with the solvent was carried out using heater PE-0316. A portable oil quality analyzer SHATOX-SX-300 was used to measure octane and cetane numbers. The recovery process was observed in the temperature range of 80-250° C using petrol such as 'Nefras-C1' and 'Nefras-C4', which possesses good hydrogen-donor capacity. The samples of morphological groups of SHW were prepared by mixing, mechanical grinding, triturating and drying of the components. Let us consider thermolysis of 100 g of food waste in a dibutylphthalate medium as an example. Food waste contained (%): hydrocarbons – 12.5; proteins – 1,6; fats – 1,2; bones, oils – 3,2, potatoes, bread. Food waste was dried, crushed and finely rubbed in a porcelain mortar. In the course of the experiments, about a dozen morphological groups of polymers containing 1000 ingredients have been studied for thermal fluidifying kinetics. Thermolysis of polymers, rubber and low-calorific natural fuels used in Russia have been studied.

The patterns of experimental kinetics are presented in Table 1.

Table 1. Kinetics of depolymerization of SHW morphological groups: temperature range is 250-260° C; reaction time is 45-60 min.

SHW morphological group	Sample weight, g	Untreated sludge mass, g	Sludge mass when weight is constant, g	Depolymerizate yield, β, %
Food waste	1.04	4.18	0.66	38
Leather	0.98	3.61	0.55	43
Rubber	1.00	3.54	0.41	59
Paper	2.00	3.00	1.16	42

It can be seen that in the conditions studied, thermal fluidifying of SHW components occurs at almost the same rate. Average depolymerize yield equal to 41 % with an average deviation of 1 % is achieved; the rate of rubber dissociation exceeded the inhibition rate of other polymers by more than 30 %; $\Delta\beta = (59-41) \cdot 100/59 = 30.5\%$.

The total rate of fuel components accumulation is determined by the rates of 2 slow kinetic stages: mass transfer of molecular hydrogen in a gaseous phase and interaction of the hydrogen donor solvent with molecular aggregates formed during plastics thermolysis. Thermodynamic characteristics of the polymers depolymerization are presented in Table 2.

Table 2. Criteria for thermal fluidifying of polymers: $\beta_p = [100-(C_p + H_p)]$ is the yield of volatile substances for combustible mass; $\beta_{p.kp} > (35-36)$; $(C/H)_p$ is the thermal fluidifying criteria of a solid polymer; $((C/H)_{kp} = (8-16))$; mark * means that the parameters of the thermal fluidifying process are outside the region of their critical values

SHW morphological groups	Content in dry SHW, %	Working fuel of moisture-free fuel, %			
		C_p	H_p	$(C/H)_p$	β_p
Plastics	8.7	67.7	9.3	7.3*	23.0
Paper, cardboard	35.1	46.2	6.2	7.4*	47.6
Food waste	18.5	53.6	7.7	7.0*	38.7
Wood	2.2	51.0	6.1	8.4	42.9
Fabric	7.6	56.1	6.8	8.3	37.1
Screening less than 16 mm	-	46.4	6.3	7.4*	47.3
Rubber, leather	6.1	77.9	6.0	13.0	16.1
SHW, total	100	57.0	7.2	7.9	35.8

It can be seen that, due to thermodynamic restrictions, a significant part of SHW mass (more than 62 % of the total mass of organic matter) is not suitable for depolymerization with a direct transformation into oil and gas products; here, the criteria $(C/H)_p$ and β_p are outside their region of their critical values. Let us determine the criterion of thermalization for a composite fuel composed according to our invention from SHW and rubber [5]:

$$(C/H)_{comp.} = 0.60 \cdot 7.9 + 0.40 \cdot 13.0 = 12.0,$$

where 0.60 and 0.40 are the feed of SHW and rubber (fractional units) into the process system. Let us accept a feed ratio of 1.5. The following technical results should be noted: the process of SHW thermolysis has been intensified, worn-out rubber has been utilized, thermochemical potential of the entire system has increased.

3. Results and Discussion

Based on the theoretical assumptions outlined above, the technological process flow is represented in Figure 2. The technological process involves the stages of feed preparation and polymers depolymerization.

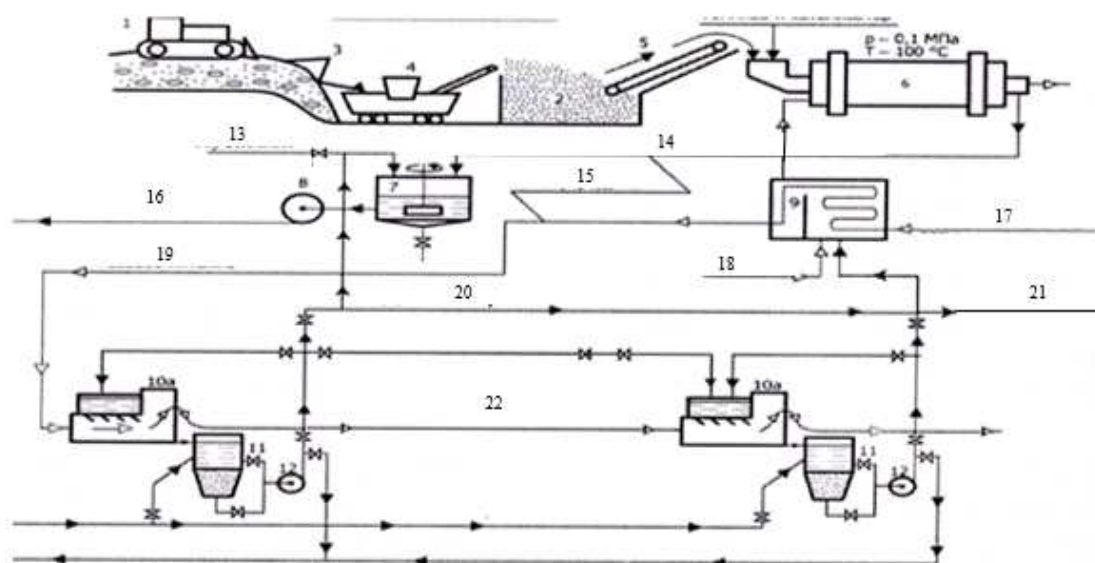


Figure 2. Technological low-waste process diagram: raw material preparation: 1 – bulldozer; 2 – raw material storage; 3 – unbalanced-throw screen; 4 – crusher; 5 – screw; 6 – grinding mill with material drying; 7 – paste preparation; 8 – paste pump; 9 – heater; chemical interaction: 10 – depolymerization/hydrogenation reactors; 11 – tank; 12 – circulation pump; 13- starting solvent; 14 – finely powdered polymer mass; 15 – intermediate products; 16 – liquid power; 17 – reducing gas; 18 – air; 19 – gas power; 20 - depolymerizat; 21 – liquid hydrocarbons; 22 – reducing gas

The technical character of the patented method [3] involves organization of a continuous technological process, including SHW receipt to a waste-processing enterprise, its preliminary separation, mechanic-chemical activation by grinding, drying, mixing with a solvent, dissolving of the formed paste at temperatures of 200-300° C, chemical processing in the hydrogen-donor organic solvent at temperatures up to 310° C and separation of the reaction mass into fractions to modify energy and motor fuels. The high power circuit further includes two recovery recycles (liquid and gaseous ($\text{CO} + \text{H}_2$)), as well as mass exchange apparatus 10 according to the invention [8]. The volume of reduced gases is almost twice less than the volume of gases in the plants for SHW thermal processing. Accordingly, operational and capital expenditures for the resource reproduction process decrease.

Further improvement of the technological process route involves equipment simplification and ecological compatibility, effectiveness of operating and capital expenditures, and fuels modification. Figure 3 shows the batch section of SHW components processing. Here, the reactor process is carried out under pressure in a two-stage tubular apparatus 3 and 4. Formation of the gasoline is performed in the subsystem: fired heater, reformer, fractionating column [4].

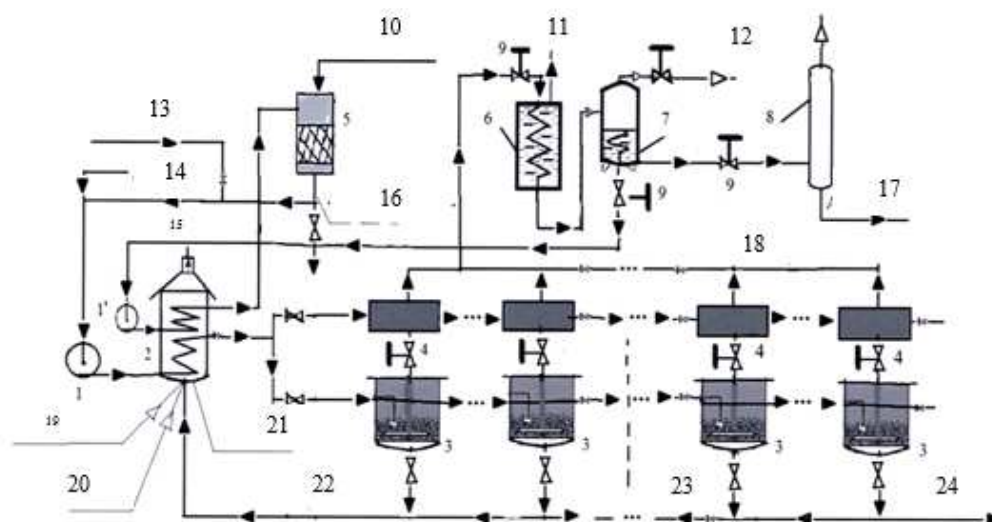


Figure 3. Batch section of SHW components processing diagram: 1 – pump; 2 – fired heater; 3 – tubular reactor, temperature of 250-300° C; 4 – tubular reactor, temperature of 500° C; 5 – reformer; 6 - 7 – cooling condenser; 8 – fractionating column; 9 – valve; 10 – superfine catalyst; 11 – water; 12 – the combustion gases; 13 - starting solvent; 14 – paste; 15 – on reforming; 16 – light hydrocarbons; 17 – motor gasoline; 18 – depolymerizer; 19 – actuator natural gas; 20 - air; 21 – cement clinker; 22 – sludge (fuel oil); 23 – sludge; 24 – liquid phase.

The proposed process is simple and reliable for processing waste in small settlements (10-15 thousand people). The production yield is as follows:

Production item	Yield, t/mass
Condensate	67
Waste metal	24
Gasoline	56
Kerosene	30
Building material	42

The resulting intermediate products such as fuel oil, kerosene and condensate are used for internal production purposes. The financial and investment attractiveness of the project are acceptable: profitability index is 2; payback period is 2.4 years; net discounted income is 60 million rubles.

4. Conclusion

As a result of patent studies of the methods and schemes, experimental and calculation studies of the theoretical foundations of chemical technology, the main objective of this article, that is, the development of source data for the design and technical and economic feasibility of the project of the pilot plant for processing SHW components by thermocatalytic depolymerization with resource reproduction of power and motor fuels, has been achieved. It should be pointed out that self-recoupment of hydrocarbon production for its internal use can be achieved by reducing energy input and obtaining sufficient yields of useful products.

5. Acknowledgments

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