

Thermo-chemical analysis and modeling of combustion of waste pyrolysis gaseous products

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Abstract. The results of the study of joint pyrolysis of various types of waste (municipal solid waste, plastic waste, etc.) are presented. Preliminarily crushed and dried wastes were fed into the pyrolysis chamber of the model experimental setup. Thermal energy required for heating raw materials and carrying out their thermal destruction was obtained by burning a part of the pyrolysis gases. The rest of these gases were removed from the pyrolysis chamber and cooled. The temperature in the pyrolysis zone was about 650 °C. Plant productivity was up to 500 kg/h. The target product was the liquid phase, which is a mixture of hydrocarbon compounds. When organizing the processes, the yield of solid carbon residue was minimized. The obtained mass ratio of the final gas/liquid products was approximately equal to 1/6. Experimental results of the analysis of the chemical composition of the gas and liquid fractions are presented. The results of modeling the combustion of pyrolysis products at different amounts of supplied air are also shown. The operating parameters at which the optimum temperature level in the pyrolysis zone is maintained are numerically determined and recommended.

1 Introduction

Waste disposal is one of the global challenges of our time, as constantly increasing waste amounts have severely negative impacts on the environment. The hazardous environmental issues include alienation of territories necessary for waste disposal, pollution of atmospheric air, land resources, surface and ground waters, etc. An obvious solution to these problems is the involvement of waste into repeated economic circulation: processing, regeneration, recovery and recycling. Improving efficiency and introducing energy and resource-saving waste disposal technologies are important scientific and technical tasks. This article examines the carbon-containing waste that is a part of typical municipal waste: plastic, polyethylene, packaging materials, etc.

Currently, waste is used to obtain heat and electricity, as well as for secondary raw materials. The most promising methods include thermal processing: pyrolysis, gasification, and combustion. Waste combustion allows to obtain thermal energy, which is then converted into electrical energy. Importantly, waste recycling results in the reduced consumption of traditional fuels, including natural gas, oil products, and coal. During gasification of waste, the main product is a mixture of combustible gases, i.e., CO, CO₂, H₂, CH₄ and others. In waste pyrolysis, the products include carbonaceous solid residue, a liquid mixture of complex hydrocarbons, and relatively small amounts of a non-

condensable gas phase. The quantitative yield of a certain product depends on the heating rate of the starting materials, the residence time in the reaction volume, and the pressure values during the conversion process. The process is carried out at very low oxygen concentrations or in its complete absence at temperatures ranging from 500°C to 800°C. The pyrolysis products have a higher energy value than the starting materials, and when burned, they can provide higher temperatures of the combustion products than when burning the starting material. Liquid pyrolysis products are used not only as an alternative fuel. Their practical importance as raw materials in chemical technologies is obvious.

The main regularities of the processes for the listed methods of thermal waste treatment are well known. Special attention is paid to the experimental and theoretical study of various aspects related to the search for the most efficient organization of processes, mainly depending on the selected processing method, chemical composition and aggregate state of the waste [1-16].

An increase in the yield of gas mixture due to the increased concentration of carbon monoxide is facilitated by the implementation of pyrolysis when supplying carbon dioxide [1]. The work [2] shows a significant effect of the presence of zeolite catalysts on the increased gas yield during pyrolysis. However, when using catalysts, it is necessary to periodically regenerate them. Studies of tire pyrolysis are of great interest [3, 4]. This technology offers an attractive increase in the yield of liquid hydrocarbons, which are valuable chemical raw

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programming from 80°C to 280°C; scanning mode of 50-600 m/z.

The experimental results were processed according to the following procedure. The sorption tube was placed into the thermal desorber. Air was removed from the tube to avoid incorrect chromatograph data arising from the thermal oxidation of the sorbent or the stationary phase used in gas chromatography. The tube was then heated to desorb organic vapors entering the column in the carrier gas stream. The carrier gas flow was directed towards the diffusion end of the tube, i.e., the marked end of the tube was located at the entrance to the column of the chromatograph. After the thermal desorber switch to the mode ready for injecting the desorbed sample into the evaporator, it switched to the standby mode. The sample was injected automatically when the chromatograph was ready. Peaks in the chromatogram were identified using the NIST MS Search 2.0 mass spectrometric library.

The obtained experimental data on the composition of pyrolysis products were used to determine the amount of air required to burn a part of the pyrolysis gases. Conditions typical for the chemically equilibrium state of products from incomplete combustion were simulated. The methodology and the calculation program presented in [17] were used here.

3 Results and discussion

The chemical composition of the condensed phase of pyrolysis products is shown in Table 1.

Table 1. The chemical composition of the condensed phase of pyrolysis products.

Chemical compound	Concentration, wt. %
Indene	17.784
Undecene-1	6.248
3,4-Dimethylstyrene	1.802
2-Methylindene	3.88
3-Methylindene	1.648
Dodecene	3.11
Naphthalene	50.218
Tridecene	2.89
2-Methylnaphthalene	1.968
1-Methylnaphthalene	4.564
Tetradecene	1.668
Acenaphthylene	1.628
Pentadecene	1.498
Acenaphthene	0.546
Hexadecene	0.542

In the condensed phase of pyrolysis products, polycyclic aromatic hydrocarbons were present in the greatest amounts (~ 82 wt. %). Unsaturated hydrocarbon compounds with double bonds were in smaller amounts (alkenes ~ 16 wt. %). The content of arenes was less than 2 wt. %.

The chemical composition of the mixture of non-condensable gases is shown in Table 2.

Table 2. The chemical composition of the mixture of non-condensable gases.

Chemical compound	Concentration, wt. %
Carbon monoxide	7.37
Methane	15.22
Carbon dioxide	11.73
Acetylene	0.20
Ethylene	29.67
Ethane	9.21
Water	0.95
Propylene	14.53
Chloromethane	0.12
Propadiene	0.12
Propane	0.66
Propine	0.23
Vinylchloride	0.11
Vinylacetylene	0.08
2-Methylpropene	2.45
1,3-Butadiene	4.88
Butylene-1	0.48
Butane	0.11
2-Butane	0.35
1,2-Butadiene	0.01
Pentene-2	0.02
Cyclopentene	0.05
Cyclopentadiene	0.56
Pentadiene	0.40
Pentane	0.24
Benzene	0.14
Hexane	0.07

A wider range of chemicals was observed in the non-condensable gas phase. Alkenes (~ 47.5 wt. %) and alkanes (~ 25.5 wt. %) were in the largest amounts. The alkadienes content did not exceed 6 wt. %. The total content of alkynes, cycloalkanes, unsaturated hydrocarbons with double and triple bonds, halogenated hydrocarbons and arenes (benzene) did not exceed 1.5 wt. %.

In the composition of pyrolysis products combusted to provide thermal energy for pyrolysis processes, the amount of condensed and non-condensable gases was ~84 wt. % and ~16 wt. %, respectively. The amount of air required for complete combustion of combustible gases was 13.22 kg air/kg fuel (equivalence ratio ER=1.0).

Table 3 shows some calculation results for the conditions of adiabatic combustion of gaseous pyrolysis products with a lack of an oxidizer.

Table 3. Parameters and composition of combustion products.

Parameters and composition	Value			
	0.3	0.4	0.5	0.6
ER	0.3	0.4	0.5	0.6
T, K	1166	1248	1590	1844
H ₂ , vol. %	4.81	14.06	9.20	5.14
CO ₂ , vol. %	30.14	29.71	23.28	18.01
CH ₄ , vol. %	6.06	0.17	<10 ⁻⁶	<10 ⁻⁸
N ₂ , vol. %	55.01	55.32	60.48	64.66
CO ₂ , vol. %	<10 ⁻³	0.01	2.89	5.31

Notably, at ER less than 0.3, the concentration of acetylene and ethylene in the products of incomplete

combustion increases. Based on the obtained results, we suggest that in order to provide thermal energy for pyrolysis processes, it is advisable to burn a part of the gases with ER values of at least 0.3. In real conditions, this ratio will depend on the intensity of heat transfer from the combustion products to the outer surface of the pyrolysis chamber and then directly to the reagents in it.

Further afterburning of products allows to obtain additional heat energy used for preheating and drying waste, as well as for heating the primary air and for other purposes. The dependence of the adiabatic combustion temperature on the equivalent ratio is shown in Fig. 2.

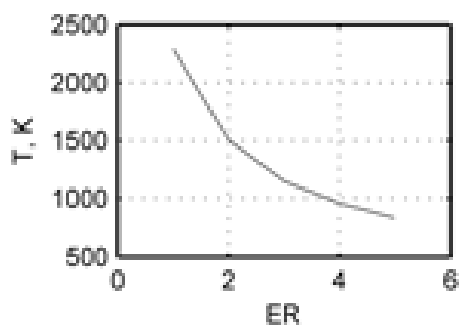


Fig. 2. Dependence of the adiabatic combustion temperature on the ER.

In after burning, the main requirement is to reduce the concentration of carbon monoxide, nitrogen oxides and unburned hydrocarbons. Therefore, after the initial incomplete combustion, secondary air should be supplied into the combustion chamber 3 (see Fig. 1) in quantities greater than stoichiometric ($ER \geq 1.6$) and then tertiary air into the mixing chamber 4 (see Fig. 1) to achieve the required temperature level at the exit. Such organization of processes ensures the conditions needed for the complete afterburning of products and reducing the emission of nitrogen oxides.

4 Conclusion

Full-scale experiments were conducted on a model setup for waste pyrolysis. For a mixture of various types of carbon-containing wastes, the total yield of the liquid fraction and the gaseous non-condensable fraction was up to 93 wt. %. The yield of the coal residue and ash was about 5 wt. % and 2 wt. %, respectively. Heat energy obtained during incomplete combustion of about 30 wt. % gaseous products was consumed for the implementation of pyrolysis processes. Since the chemical composition of the pyrolysis products and the optimal modes of organizing the processes depend on the chemical and aggregate state of the starting materials, it is necessary to control temperature levels in the thermal decomposition chamber, combustion chamber and mixing chamber, and to regulate the air supply into these chambers.

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