

SCTMG 2023**International Scientific Conference "Social and Cultural Transformations in the Context of Modern Globalism"****SOCIAL AND ECOLOGICAL ROLE OF SOLID MUNICIPAL WASTE RECYCLING**

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Abstract

The article considers heterogeneous chemical-technological processes in the treatment of solid municipal waste. In the course of heterogeneous chemical-technological process (HTP) there are two elementary processes - diffusion of substances in one phase to the interface or from it and chemical reaction inside one of the phases. Depending on the fact in which of these processes the reaction occurs determines the rate of CTP, the latter is divided by the area of flow, i.e. in the diffusion region or in the kinetic region. Methods and techniques of CTP intensification in these areas are quite different. Knowledge of the process flow region is especially important for analysis and control of heterogeneous-catalytic processes, which determine the quality of functioning of waste processing industries. The degree of CTP perfection is determined by the final yield of the product of solid municipal waste processing. The developed model of chemical-technological processes allows, at its use, to improve technical indicators of quality of the complex on processing of solid municipal waste.

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1. Introduction

The problem of solid municipal waste (SMW) management in Russia is of a national scale. About 60 million tonnes of solid waste are generated annually, of which no more than 15% is recycled. The total area of landfills and dumps has reached more than 4 million hectares, and this area is annually increasing by 300-400 thousand hectares (Vaisberg et al., 2019). At the same time, the adopted "Concept of Extended Producer Responsibility", (2021) sets the task to reduce the amount of waste sent to landfill by 50% by 2030.

2. Problem Statement

To fulfil this task it is necessary to significantly improve the existing methods of solid municipal waste processing, with obtaining products of energy utilisation and secondary material resources. Maximisation of output products requires the development of an adequate model describing chemical and technological processes of solid municipal waste processing.

3. Research Questions

The research was based on the analysis of laboratory data of technical quality indicators that determine the efficiency of TPO processing:

- i. the degree of transformation of raw material (waste) components;
 - ii. product yields for the respective components;
 - iii. the speed of the process and its selectivity;
- consumption coefficients for raw materials (waste).

4. Purpose of the Study

When developing a model of MSW processing on the basis of chemical-technological processes, the most important is the characterisation of the aggregate state of the feedstock. According to this feature, homogeneous processes are distinguished, when all interacting substances are in a gaseous or liquid state with no interface between them, and heterogeneous processes, in which reacting substances are initially in different aggregate states (Osipov, 2019).

If the reactants are well mixed before entering the reaction, the rate of homogeneous processes is determined by the rate of direct chemical transformation of substances. In heterogeneous processes, chemical reactions are usually accompanied by purely physical intermediate steps that determine the rate or influence the observed rate of the process.

5. Research Methods

In the course of heterogeneous CTP, two elementary processes can be distinguished - diffusion of substances in one phase to or from the interface and chemical reaction within one of the phases. Depending on which of these processes determines the rate of CTP, the latter are divided by the region of

flow, i.e. in the diffusion region or in the kinetic region (Hermawansyah, 2018). The methods and techniques of CTP intensification in the mentioned areas are quite different. Knowledge of the process flow region is especially important for analysing and controlling heterogeneous-catalytic processes that determine the quality of functioning of waste processing industries (Kascheev & Kazakov, 2021).

6. Findings

The technological quality indicators (TQI), determining the efficiency of recycling of MSW should include:

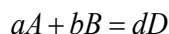
- i. the degree of transformation of raw material (waste) components;
- ii. product yields for the respective components;
- iii. the speed of the process and its selectivity.
- iv. consumption coefficients for raw materials (waste);

6.1. Degree of transformation

Process perfection in terms of the most complete recycling of MSW is assessed by the degree of conversion (CoC).

SP is the ratio of the amount (mass, volume) of one of the reactants that has entered the reaction to the initial amount (mass, volume) of that reactant.

For example, for the reaction



the degree of transformation of substance X is calculated according to the relations:

$$X_A = (m_{A,0} - m_A) / m_{A,0} = (n_{A,0} - n_A) / n_{A,0} = (\gamma_{A,0} - \gamma_A) / \gamma_{A,0}$$

$$X_B = (m_{B,0} - m_B) / m_{B,0} = (n_{B,0} - n_B) / n_{B,0} = (\gamma_{B,0} - \gamma_B) / \gamma_{B,0}$$

where $m_{A,0}$, $m_{B,0}$, $n_{A,0}$, $n_{B,0}$, $\gamma_{A,0}$, $\gamma_{B,0}$ are mass, number of moles and volume of reactants A and B at the beginning of the process;

m_A , m_B , n_A , n_B , γ_A , γ_B - same at the end of the process.

If reagents A and B are taken in stoichiometric ratio, then $X_A = X_B$

The degree of conversion of a reactant taken in excess of the stoichiometric ratio is always lower than for a reactant supplied in deficiency. If α_B is the excess of B over the stoichiometric ratio, then

$$X_A = \alpha_B * X_B$$

herewith

$$\alpha_B = n_{B,0} * a * b / n_{A,0}$$

If the reaction proceeds without volume change, the concentration (C , mol/m³) of the reactant or its volume fraction (W , %) at the beginning and end of the process are equal:

$$C_{A,0} = n_{A,0} / \gamma \quad C_A = n_A / \gamma$$

For reactions occurring with a change in volume

$$X_A = (C_{A,0} - C_A) / (C_{A,0} - \varepsilon_A * C_A)$$

where ε_A is the relative change in the volume of the reaction mixture at full conversion of reactant A.

For interfacial mass transfer processes (evaporation, condensation, adsorption, desorption, etc.), the degree of transformation is called the degree of interfacial transition, e.g. the degree of adsorption, the degree of condensation, etc (Kascheev et al., 2020).

6.2. Product yield

For complex (parallel, sequential, etc.) reactions, along with the degree of transformation of initial substances, the concept of "product yield" is used (Lopatin et al., 2022).

Product yield F is the ratio of actually obtained product n_ϕ (or m_ϕ) to its maximum amount n_{MAKC} (or m_{MAKC}) calculated from the stoichiometric equation of the reaction when the degree of transformation of the initial reagents is equal to 1.

$$\Phi_\phi = n_\phi / n_{\text{MAKC}} = m_\phi / m_{\text{MAKC}} \quad (1)$$

If two or more substances are involved in a reaction, e.g. $A + B \rightarrow D$, the yield of the target product D is distinguished for the starting substance A ($F_{D(A)}$) and for the substance B ($F_{D(B)}$). If A and B are not contained in a stoichiometric ratio in the starting mixture, $F_{D(A)}$ is not equal to $F_{D(B)}$.

For simple reactions (i.e., in the absence of parallel or sequential transformations), the product yield for any component of the feedstock (waste) is numerically equal to the degree of transformation of this component (Kascheev et al., 2019).

For irreversible reactions, the maximum actual yield $F_\phi \text{ max}$ is 1. For reversible reactions, the starting substance is not completely transformed into the product, and if in formula (1) instead of n_ϕ substitute the amount of product obtained under equilibrium conditions n^* , then $F_\phi \text{ max} < 1$. This yield is called equilibrium F^*

$$\Phi_{\phi\text{MAKC}} = n^* / n_{\text{MAKC}} = \Phi^*$$

To characterise the degree of approximation of a reversible process to equilibrium, the so-called "yield from theoretical" or "yield from equilibrium" is used in practice, which is equal to the ratio of the quantity of the actually obtained product n_ϕ to the quantity that would have been obtained if the process had reached the equilibrium state n^* .

$$\Phi_n = n_\phi / n^* = \Phi_\phi / \Phi^*$$

The output from the equilibrium most objectively characterises the perfection of the process in terms of the efficiency of use of resources of the second kind (waste).

Product yield is expressed in fractions of a unit or in per cent. This indicator largely reflects the degree of perfection of the technological process, raw material costs per unit of product and economic performance of the complex for recycling of MSW.

6.3. CTP rate

To determine the time required to achieve a product yield or a given degree of transformation of the initial reagent (waste), it is necessary to know the rate of the technological process (Konovalov & Yakubovskaya, 2022).

The rate of a chemical-technological process is expressed by the change in the amount of a component reacted or formed as a result of a chemical reaction per unit of time in a unit of reaction volume V (for homogeneous CTP) or on a unit of interface surface (for heterogeneous CTP).

If no substance is exchanged with the environment during the process, then the average rate of consumption of input material (waste) or product formation over the time interval $\Delta\tau = \tau_2 - \tau_1$, is generally equal:

$$U = (n_2 - n_1) / v(\tau_2 - \tau_1) = \Delta n / v\Delta\tau$$

where n_1, n_2 are the number of moles of the substance at times τ_1 and τ_2 respectively;

v is the average volume of the reacting mixture.

The average velocity is equal to the intensity of the process. When $\Delta\tau = 0$, the instantaneous or true velocity corresponding to a particular moment of time is obtained. The instantaneous velocity of CTP is expressed by the ratio

$$U = \lim \Delta n / v\Delta\tau = + / - dn / vd\tau \quad (2)$$

It should be noted that expression (2) works if the following conditions are met: a) the reaction volume remains constant; b) the volume can be considered closed.

Closed or confined volumes correspond to conditions where the reacting system does not exchange substances with the environment. This is usually the case for processes in batch reactors.

If the rate is to be determined by the reaction product, expression (2) is used with a plus sign, if by the starting substance - with a minus sign.

Let us obtain a simpler equation for CTP proceeding at constant volume. Taking into account that $n_i / v = C_i$, i.e. equal to the concentration of the substance, at constant volume we have:

$$U = + / - dC_i / d\tau$$

For processes with gaseous matter, it is convenient to express the velocity in terms of the change in partial pressures P_i , of the reacting components of the mixture.

$$U' = + / - dP_i / d\tau$$

The rate can also be expressed through the change in the degree of transformation:

$$U'' = + / - dX_i / d\tau$$

The relationship between U , U' and U'' is described by the relation:

$$U = U' / (RT) = C_{i,0} * U''$$

where R is the universal gas constant equal to 8.314 J/mol*K;

T - temperature, K;

$C_{i,0}$ - initial concentration of i - component.

For heterogeneous CTP, when the reaction takes place at the interface, the rate should be expressed through the unit of interfacial surface S

$$U = + / - 1d_{ni} / Sd\tau$$

At that, if the velocity is expressed as

$$U_i = + / - 1d_{ni} / v_i d\tau = \alpha dC_B / f d\tau$$

where v_i is the stoichiometric coefficient at the corresponding reagent,

then it will have the same value regardless of which of the reactants it is attributed to. Such a value of the rate is called invariant.

CTP speed in general case depends on speeds of physical and chemical processes, which in turn are determined by hydrodynamic parameters of reagents (waste components) movement, mixing conditions, diffusion, concentrations, pressure, temperature and other factors influencing mass and heat transfer.

On this basis, in the most general form, the formula for calculating the process speed can be represented as:

$$U = + / - dC / d\tau = K \Delta C$$

where K is the process speed coefficient;

ΔC is the driving force of the process.

The process rate coefficient depends on the process area and is a function of the rates of forward (to_1), reverse (to_2) and side (to_n) reactions, the diffusion coefficients of initial reactants to the interface ($D_1, D_2 \dots$) and reaction products from the interface ($D_1^*, D_2^* \dots$):

$$K = f(k_1, k_2, k_n, \dots, D_1, D_2, \dots, D_1^*, D_2^* \dots) \quad (3)$$

Knowing the area of the process flow, the operators of the MSW processing complex select the main parameters that most strongly influence the process speed. In this case the expression for calculation of the process speed coefficient (3) is simplified. Thus, for homogeneous or heterogeneous processes occurring in the kinetic region, K depends only on the rate constants of the main and side reactions:

$$K = f(k_1, k_2, k_n, \dots)$$

For heterogeneous processes occurring in the diffusion domain, the rate-determining influence on the velocity is exerted by diffusion coefficients of gas or liquid inside the denser phase (for example, in the pores of solid matter of municipal waste):

$$K = f(D_1, D_2, \dots, D_1^*, D_2^* \dots)$$

The driving force of a process (ΔC) is in general a complex function of current ($C, C_{l2} \dots$) and equilibrium ($C_1^*, C_2^* \dots$) concentrations of reacting substances, equilibrium constant K_p and other parameters. The type of function depends on the type of reaction and the area of the process.

6.4. Selectivity

Selectivity (selectivity) is an important characteristic of processes in which, along with the main reaction of the target product formation, side parallel or sequential reactions occur with the formation of less valuable products (or undesirable ones).

A distinction should be made between finite total (integral) selectivity and instantaneous (differential) selectivity.

The total selectivity φ_c is defined as the ratio of the amount of starting substance transformed into the target product of waste utilisation to the total amount of reacted starting substance (waste). For example, for parallel reactions $Aa \rightarrow Bb \rightarrow Dd$, the target product of which is substance B, the total selectivity $\varphi_{B,c}$ is expressed as:

$$\varphi_{B,c} = a * n_B / b(n_{A,0} - n_A) = a / b * n_B / [(a / b) * n_B + a / d) * n_D]$$

The relationship between the degree of transformation X_A , the product yield $F_{B(A)}$ and the total selectivity $\varphi_{B,c}$ is determined from the relations:

$$X_A = (n_{A,0} - n_A) / n_{A,0}$$

$$\Phi_{B(A)} = a * n_B / (b * n_{A,0})$$

$$\varphi_{B,c} = \Phi_{B(a)}$$

The instantaneous selectivity φ_{MTH} is measured by the ratio of the invariant rate of formation of the target product to the invariant rate of consumption of the starting reagent used to form all reaction products. In other words, this selectivity is equal to the ratio of the rate of the main reaction to the total rate of the process expressed in terms of the amount of starting reagent.

$$\Phi_{B,MTH} = U_B / U_A$$

$\Phi_{B,MTH}$ makes sense of the instantaneous yield of the target product.

Instantaneous selectivity can also be estimated through the ratio of the rates of formation of the target and by-product:

$$\Phi_{B,MTH} = U_B / U_D$$

Total selectivity is equal to the sum of all instantaneous outputs.

6.5. Expense ratios

Consumption coefficients characterise the costs of raw materials for the production of waste products.

The consumption factor is the ratio of the amount of raw materials consumed to carry out CTP to the amount of the target product obtained.

The theoretical flow coefficient is calculated from the stoichiometric equation of the main reaction, taking into account the content of the starting reagent in the raw material. For example, for the reaction $aA \rightarrow bB$, the theoretical consumption factor η_T to obtain product B is determined by the ratio:

$$\eta_T = aM_A / (bM_B \omega_{A,C})$$

where M_A , M_B are the molecular masses of reactant A and product B;

$\omega_{A,C}$ - mass fraction of component A in the raw material, %.

In practice, the calculation of consumption coefficients (η_n) is performed taking into account the degree of transformation of the initial reagent XA, product yield $F_{B(A)}$ and selectivity φ_c :

$$\eta_{II} = \eta_m / (X_A \varphi_{Bc}) = \eta_m / \Phi_{B(A)}$$

The practical consumption coefficient is always higher than the theoretical one. When solving the problem of improving the efficiency of recycling of MSW, it is necessary to reduce the ratio η_n / η_m without increasing the cost of the product. This is achieved by increasing the degree of transformation, selectivity and, as a consequence, the yield of the waste treatment product.

7. Conclusion

The developed model of chemical-technological processes allows, if used, to improve technical indicators of solid municipal waste processing quality. It is recommended to subject to energy utilisation of solid municipal waste the wastes that have undergone extraction of secondary material resources in the amount of not less than 15%, as well as extraction of compostable fraction. Processing of 4 tonnes of waste gives approximately the same amount of energy as one tonne of oil.

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