

Mathematical Modeling for the Development of Equipment for Thermochemical Processing of Wood Waste in to Dimethyl Ether

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Abstract. The paper describes the process of thermochemical wood waste processing in to dimethyl ether. The physical picture of the process of waste wood recycling was compiled and studied and the mathematical model in the form of differential and algebraic equations with initial and boundary conditions was developed on its basis. The mathematical model allows to determine the optimum operating parameters of synthesis gas producing process, suitable for the catalytic synthesis of dimethyl ether and to calculate the basic constructive parameters of the equipment flowsheet.

1. Introduction

During the development of new equipment there are always technological and engineering calculations to be done. Performing of these tasks in the modern world is unthinkable without the use of methods and means of mathematical modeling of developed processes. The implementation of the mathematical model allows: to solve the problem of choosing the optimal construction of the equipment and its main dimensions; to identify effective operational parameters of the process; to improve existing and develop new types of equipment [1]. The use of mathematical modeling is especially important in the development of new technological processes. The process of producing dimethyl ether at the thermochemical processing of wood waste can be referred to one of the new technologies. It should be noted that such a development direction of the wood raw material processing technologies is very important. This approach solves the environmental problem of the volume of waste wood and raw material reduction and a resource problem being as a result of dimethyl ether [2]. Dimethyl ether can be used as a motor fuel, fuel for power plants and as an intermediate for the synthesis of gasoline with improved environmental characteristics and minimum content of undesirable impurities [3].



During the development of new technologies due to their complexity and the danger it is often advisable to carry out their theoretical analysis and mathematical modeling. In such cases, the use of computer modelling based on the process of developed mathematical model is irreplaceable.

Based on the foregoing, the aim of the paper is forming a mathematical model of the process of thermochemical processing of wood waste in to dimethyl ether, to obtain data on the structural dimensions of the equipment and technological operation. The characteristics of wood waste, gasifying agent species, catalyst species, temperature and process pressure are taken as initial data.

2. Description and formalization of the process

In order to ease and simplify the development of a mathematical model, the installation scheme for processing wood waste in to dimethyl ether was charted (figure 1). The scheme reflects the physical processes that occur during the plant operation and basic operational parameters.

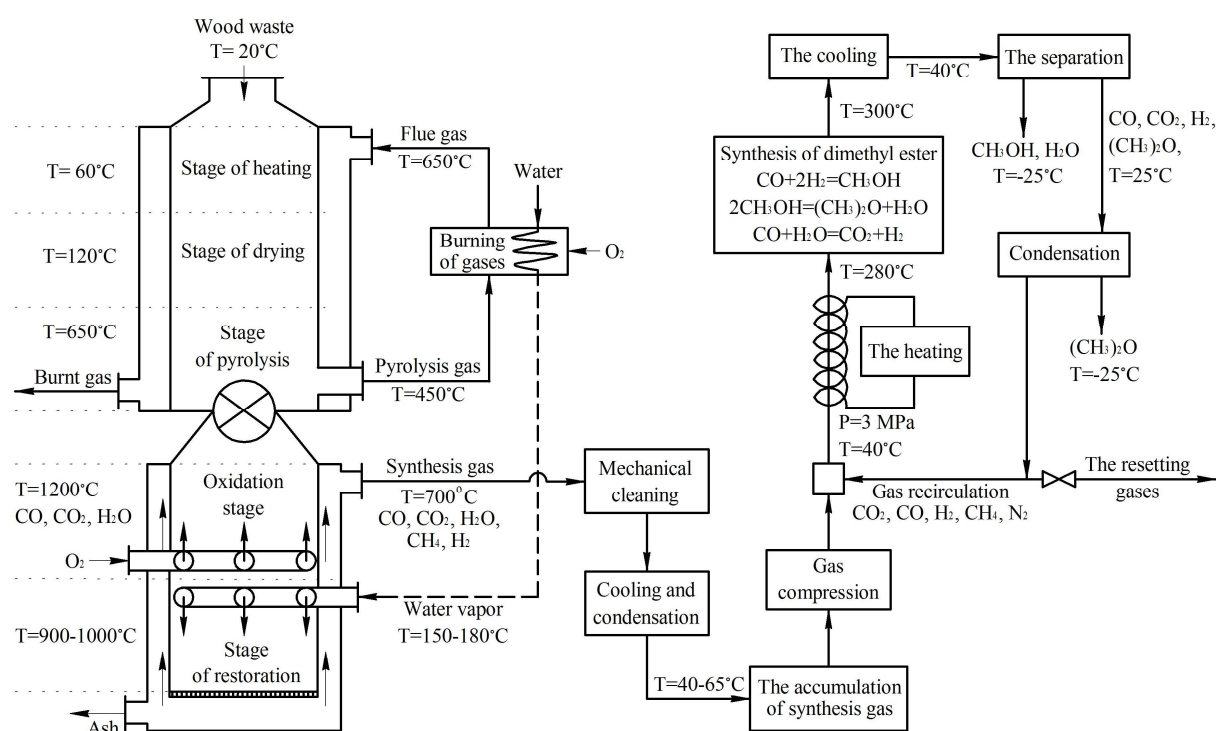


Figure 1. The plant layout of wood waste processing in to dimethyl ether and the physical picture of the technological process

We can distinguish two main blocks on the layout (figure 1). The first block characterizes the wood waste thermochemical processing in to synthesis gas by combining the pyrolysis and gasification processes [4, 5]. The second block includes the one-stage process of catalytic synthesis of dimethyl ether from synthesis gas obtained in the first stage.

We'll consider the process in more details. Wood waste successively passes through different phases after entering the installation: heating, drying, pyrolysis, oxidation and reduction step (synthesis gas stage) [6]. Further, to achieve the required parameters the formed synthesis gas passes the steps of purification from the mechanical impurities, is subjected to cooling and condensation of water vapour. As a result, the raw material - the synthesis gas is formed in the first block during thermal processing of waste wood which is then used for one-step dimethyl ether synthesis catalyst.

A catalyst mixture of a methanol synthesis (Katalco-58, composition: $\text{CuO} / \text{ZnO} / \text{Al}_2\text{O}_3$) and methanol dehydration ($\gamma\text{-Al}_2\text{O}_3$) is used as a catalyst for the synthesis of dimethyl ether [7]. The catalyst mixture is placed in three layers: the first layer - Katalco-58; second layer - a mixture of

Katalco-58 and $\gamma\text{-Al}_2\text{O}_3$; a third layer of $\gamma\text{-Al}_2\text{O}_3$. During the process of catalytic synthesis the reactions of joint formation as methanol so dimethyl ether are occurred. This process is exothermic and proceeds with decrease in volume, that is why a constant maintaining of the temperature and pressure within the required limits is needed [8, 9].

Next, the resulting product mixture leaving the synthesis reactor is cooled and separated into two phases: a liquid phase and a vapour one. The liquid phase consists of methanol and water, and the gas-vapour phase has dimethyl ether, which is released in the condensation stage. Not condensed gases are mixed with initial synthesis gas and are fed into the reactor again.

The description of the process shows that the processes of thermochemical processing of wood waste in to the dimethyl ether together are complicated for mathematical description. This is due to the complex chemical structure of wood waste and the influence of catalytic synthesis process of dimethyl ether as the component composition of the synthesis gas [10]. Therefore the receiving of a good quality synthesis gas has a very high value as a raw material for the synthesis of dimethyl ether. As a result, for the constructive mathematical description we must enter the following key assumptions:

- polydisperse wood particle system is considered as one particle of cylindrical shape, with the volume equal to the volume of the loaded material. Meanwhile the porosity of the layer is replaced with a porosity of the particles;
- when considering the heating step, drying and pyrolysis processes the imposition of time is not considered. Each stage is considered in sequence [6];
- wood pyrolysis process is described by the decomposition scheme on the main components of wood - coal and gas (figure 2). The mechanism of the thermal decomposition assumes, that pyrolysis of wood is held in two reactions. One of them is an endothermic reaction of gas formation, while the other - of the intermediate residue which is further decomposed into carbon and gas [11]. The reaction rate constant and the proportion of the substance components are reported in the literature [12]
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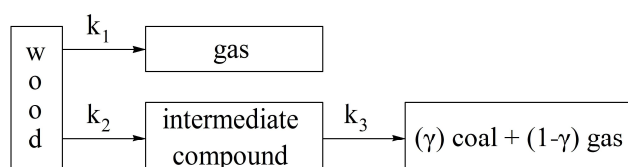


Figure 2. The mechanism of thermal decomposition of wood

- during the pyrolysis external volume of cylindrical particle remains constant, but the number of pores is increased, due to convective heat and mass transfer [13];
- we assume that there are only heterogeneous reactions of carbon and the oxidizing agent intercation occur in the oxidizing zone:

$$C + O_2 = CO_2, \quad 2C + O_2 = 2CO;$$
- considering the high temperature on the oxidation stage we assume that the temperature of the coal is equal to gas temperature. This determines the initial and boundary conditions of the reduction stage;
- the molecular diffusion is neglected in the reduction zone [1];
- recovery zone is defined by the following set of reactions [14]:

$$C + CO_2 = 2CO; \quad C + H_2O = CO + H_2;$$

$$CO + 2H_2O = CO_2 + 2H_2 \quad CO + H_2O = CO_2 + H_2$$
- final component composition of the synthesis gas is taken in the form of CO , CO_2 , H_2 and H_2O ;
- steam and gas mixtures obey the ideal gas law;
- dimethyl ether synthesis on catalyst layers occurs only from carbon monoxide and hydrogen;

- changes do not occur in the chemical composition of the catalyst.

In view of the assumptions and hypothesis the mathematical model is described by the system of simplified differential equations of thermal and mass conductivity.

3. Description of mathematical model

Considering the description of the installation's scheme and physical picture of technological process (figure 1) at first the process unit that includes a complex of processes of warming, drying and pyrolysis of conditional cylindrical particle is considered. Change in the temperature of the particles at these processes is described by the differential equation of heat transfer [14]

$$c_{part} \cdot \rho_{part} \cdot \frac{\partial T_{part}}{\partial \tau} = \frac{\partial}{\partial l} \left(\lambda_{ef} \cdot \frac{\partial T_{part}}{\partial l} \right) + q_{part} \quad (1)$$

The initial and boundary conditions are formulated to solve the differential equation (1):

$$T_{part}(0, l) = T_{part.pr} \quad (2)$$

$$-\lambda_{part} \frac{\partial T_{part}}{\partial l} \Big|_{l=0} = \alpha \cdot (T_g - T_{part}) \quad (3)$$

where T_g – gas temperature is determined from the following equation

$$T_g = \frac{q \cdot C_g}{\rho \cdot c} \quad (4)$$

When considering the drying step, the heat flux (q_{evap}) to the evaporation of moisture is given by

$$q_{evap} = r \cdot j = r \cdot \frac{m_{part}}{F} \cdot \frac{\partial W_{part}}{\partial \tau} \Big|_{l=0} = r \cdot \frac{\rho_{part}}{f_{part}} \cdot \frac{\partial W_{part}}{\partial \tau} \Big|_{l=0} \quad (5)$$

As a result of some transformations the drying step will be described by a system of differential equations

$$c_{part} \cdot \rho_{part} \cdot \frac{\partial T_{part}}{\partial \tau} = \frac{\partial}{\partial l} \left(\lambda_{ef} \cdot \frac{\partial T_{part}}{\partial l} \right) + r \cdot \varepsilon \cdot \frac{\partial W_{part}}{\partial \tau} \quad (6)$$

$$\frac{\partial W_{part}}{\partial \tau} = \frac{k_p}{\rho_0} \left(\frac{\partial^2 P_{part}}{\partial l^2} \right) \quad (7)$$

The pressure inside the particle is determined depending on the temperature of the particle, according to the equation [1]

$$P_{part} = \exp \left(A - \frac{B}{T_{part}} \right) \cdot \log_{10.6} \frac{W_{part}}{3.27 - 0.015 \cdot (T_{part} - 273)} \quad (8)$$

The initial and boundary conditions for solving the system of equations (6)÷(7) can be written as follows

$$W_{part}(0,l) = W_{part.pr} \quad (9) \quad P_{part}(0,l) = P_{atm} \quad (11)$$

$$T_{part}(0,l) = T_{part.pr} \quad (10) \quad P_{part}|_{l=L} = P_{part} \quad (12)$$

and the boundary temperature conditions are written similar to the expression (3).

Description of the pyrolysis step is carried out based on the taken scheme of thermal wood decomposition (figure 2). As a result, the equation of mass changes of the substance can be written in the following form [4].

$$\text{For the initial wood:} \quad \frac{\partial m_w}{\partial \tau} = (-k_1 + k_2) \cdot m_w \quad (13)$$

$$\text{For intermediate substance:} \quad \frac{\partial m_{i.c.}}{\partial \tau} = k_2 \cdot m_w - k_3 \cdot m_{i.c.} \quad (14)$$

$$\text{For coal:} \quad \frac{\partial m_{coal}}{\partial \tau} = \gamma \cdot k_3 \cdot m_{i.c.} \quad (15)$$

From the assumptions the volume of the solid phase particles is determined by the equation

$$V_{sol} = V_{pr} - V_{voi} \quad (16)$$

Changes in the mass per volume unit of the gas phase can be expressed by convection and pyrolysis reactions

$$\frac{\partial(m_g \varepsilon)}{\partial \tau} + \frac{\partial(v_g m_g)}{\partial l} = (1 - \gamma) \cdot k_3 \cdot m_{i.c.} \quad (17)$$

where ε – is a porosity of material, that is determined from the expression [12]

$$\varepsilon = 1 - \left(1 - \varepsilon_w^0\right) \cdot \frac{m_w + m_{coal}}{m_w^0} \quad (18)$$

Gas flow rate (v), is defined by Darcy's law [15]

$$v = -\frac{B_{part}}{\mu} \cdot \frac{\Delta P}{L} \quad (19)$$

In view of the equation (17) and the assumption that the gases behave as an ideal gas, we obtain the equation of gas pressure changes

$$\frac{\partial}{\partial \tau} \left(\frac{\varepsilon \cdot P_g}{T} \right) = \frac{\partial}{\partial l} \left(\frac{B \cdot P_g}{\mu T} \right) + \frac{R}{M_g} \cdot S_g \quad (20)$$

where mass formation of the gas (S_g) [4]:

$$S_g = (1 - \gamma) \cdot k_3 \cdot m_{i.c.} \quad (21)$$

The equation of energy conservation for the pyrolysis step can be written as

$$\begin{aligned} & \left(c_w^0 \cdot m_w + c_w^0 \cdot m_{i.c.} + c_{coal} \cdot m_{coal} + \varepsilon \cdot c_{Pg} \cdot m_g \right) \cdot \frac{\partial T}{\partial \tau} + c_{Pg} \cdot m_g \cdot v \frac{\partial T}{\partial l} = \\ & = \frac{\partial T}{\partial l} \left(\lambda_{part} \frac{\partial T}{\partial l} \right) - (k_1 \cdot \Delta \alpha_1 + k_2 \cdot \Delta \alpha_2) \cdot m_w + k_3 \cdot m_{i.c.} \cdot \Delta \alpha_3 \end{aligned} \quad (22)$$

where α – heat transfer coefficient, defined by Nusselt number [1]. The thermal conductivity coefficient (λ) is defined as the sum of the thermal conductivity of solid and volatile substances, considering the emission of heat transmitted through the pores [10]

$$\lambda_{part} = (1 - \eta) \cdot \lambda_w^0 + \eta \cdot \lambda_{coal} + \varepsilon \cdot \lambda_g + \frac{13.5 \cdot \sigma \cdot T^3 \cdot d_{por}}{e} \quad (23)$$

To solve the system of equations (13)÷(15), (17), (20) and (22) the initial conditions are formulated (24)÷(29). The boundary conditions for the pressure (30) can be written on the basis of the ideal gas law [4], and the boundary temperature conditions are written similar to the expression (3).

$$m_w(0, l) = m_w^0 \quad (24) \quad T_{part}(0, l) = T_{part.pr} \quad (28)$$

$$m_{i.c.}(0, l) = 0 \quad (25) \quad P_{part}(0, l) = P_{atm} \quad (29)$$

$$m_{coal}(0, l) = 0 \quad (26) \quad \left. \frac{\partial P_g}{\partial l} \right|_{l=L} = v \cdot \frac{\partial (v \cdot m_g)}{\partial l} \quad (30)$$

$$m_g(0, l) = 0 \quad (27)$$

When considering the oxidation step, taking into account the assumptions, the equation changes of coal mass and concentrations of the reaction components can be written as

$$\frac{\partial C_i}{\partial \tau} = -k_i \cdot C_i \quad (31)$$

$$\frac{\partial m_{coal}}{\partial \tau} = -m_{coal} \cdot \sum_{m=1}^z k_i \quad (32)$$

wherein

$$\frac{\partial T_{coal}}{\partial \tau} = \frac{\partial T_g}{\partial \tau} \quad (33)$$

Then the equation of energy conservation for coal can be written as follows:

$$\rho_{coal} \cdot c_{coal} \cdot \frac{\partial T_{coal}}{\partial \tau} = \sum_{i=1}^z (q_i \cdot k_i (C_{i0} - C_i)) \quad (34)$$

To solve the system of equations (31)÷(34) the following points are taken:

- initial conditions:

$$T_g = T_{coal} = T_{part.pr} \quad (35)$$

$$m_{coal} = m_{coal0} \quad (36)$$

$$C_{(CO_2)} = 0 \quad (37)$$

$$C_{(CO)} = 0 \quad (38)$$

$$C_{(O_2)} = C_{(O_2)pr} \quad (39)$$

- boundary conditions:

$$\left. \frac{\partial T_{coal}}{\partial y} \right|_{y=0} = T_{coal} \quad (40)$$

$$\left. \frac{\partial C_i}{\partial y} \right|_{y=0} = C_{i0} \quad (41)$$

$$\left. \frac{\partial m_{coal}}{\partial y} \right|_{y=0} = m_{coal0} \quad (42)$$

The reduction step based on the assumptions, is described by the following system of equations of thermal and mass conductivity [15]

$$w_{gs} \cdot \frac{\partial C_i}{\partial y} = -k_i \cdot C_i \quad (43)$$

$$w_{coal} \cdot \frac{\partial m_{coal}}{\partial y} = -m_{coal} \cdot \sum_{m=1}^{\bar{z}} k_i \quad (44)$$

$$\rho_{gs} \cdot c_{gs} \cdot w_{gs} \cdot \frac{\partial T_{gs}}{\partial y} = -\alpha_{gs} \cdot (T_{coal} - T_{gs}) \cdot f + \sum_{i=1}^{\bar{z}} (q_i \cdot k_i \cdot (C_{i0} - C_i)) \quad (45)$$

$$\rho_{coal} \cdot c_{coal} \cdot w_{coal} \cdot \frac{\partial T_{coal}}{\partial y} = \alpha_{gs} \cdot (T_{coal} - T_{gs}) \cdot f - \sum_{i=1}^{\bar{z}} (q_i \cdot k_i \cdot (C_{i0} - C_i)) \quad (46)$$

To solve the system of equations (43)÷(46) following initial conditions are accepted

$$T_{coal} = T_{coal.pr} \quad (47) \quad C_{(O_2)} = C_{(O_2)pr} \quad (51)$$

$$T_g = T_{g.pr} \quad (48) \quad C_{(H_2)} = 0 \quad (52)$$

$$C_{(CO_2)} = C_{(CO_2)pr} \quad (49) \quad C_{(H_2O)} = 0 \quad (53)$$

$$C_{(CO)} = C_{(CO)pr} \quad (50) \quad m_{coal} = m_{coal.pr} \quad (54)$$

and the boundary conditions of temperature and mass are written in the form of

$$-\lambda_{coal} \frac{\partial T_{coal}}{\partial y} + v_{gs} \frac{\partial T_{coal}}{\partial y} + \sum_{i=1}^{\bar{z}} q_i \cdot k_i \cdot (C_{i0} - C_i) = T_{coal.pr} \quad (55)$$

$$\left. \frac{\partial T_{coal}}{\partial y} \right|_{y=0} = \left. \frac{\partial T_g}{\partial y} \right|_{y=0} \quad (56)$$

$$v_{coal} \frac{\partial m_{coal}}{\partial y} = - \sum_{i=1}^z k_i \cdot C_i \quad (57)$$

The process of producing the dimethyl ether from synthesis gas, according to the process description proceeds on a mixture of various catalysts. Based on that the differential equation of heat and material balance, reflecting the change in flow key components: CO , CO_2 , CH_3OH , C_2H_6O on various catalysts can be written as [9]:

$$\frac{dX_i}{d\tau} = \omega_{ik} (1 - \varepsilon_k) \quad (58)$$

$$\frac{dT}{d\tau} = \frac{-1}{\sum X_i c_{pi} (\sum \Delta H_{rk} \omega_k (1 - \varepsilon_{mk}) + \sum \Delta H_{rk} \omega_k (1 - \varepsilon_k) - KS_x (T - T_x))} \quad (59)$$

The initial conditions for solving the system of equations (58)÷(62) take the form

$$\tau = 0 \quad (60) \quad C_i^{sur} = C_{i0} \quad (61) \quad T = T_0 \quad (62)$$

and the condition of equality of the substance transfer rate to the chemical reaction rate on the catalyst can be written as [9]

$$\beta_i S_k (C_i^{sur} - C_i) = (1 - \varepsilon_k) \omega_{ik} \quad (63)$$

Reaction rate is defined by the partial pressure of each component in the mixture.

4. Conclusions

The developed mathematical description of the process of thermochemical processing of wood waste in to the dimethyl ether is presented in the form of the main differential and algebraic equations of heat and mass transfer with the initial and boundary conditions. To simulate the process a numerical method of the decomposition of differential equations on finite-difference (mesh) schemes is used and a calculation algorithm is developed [6]. Modeling based on this mathematical description allows: to determine the optimum operating parameters of the process for producing synthesis gas suitable for catalyst synthesis of dimethyl ether; calculate the basic constructive parameters of technological scheme equipment. The following estimates can be attributed to the constructive parameters of equipment: adjusted volume of the pyrolysis chamber, which calculations are based on the productivity of equipment; the height of the pyrolysis chamber, which is determined depending on the time of the pyrolysis process; volume of the reaction chamber of the gas generator associated with the volume of the pyrolysis chamber; Further, knowing the volume of the reaction chamber we can calculate its diameter, height, number of nozzles, the size of the ash separation, etc.

It should be noted that the use of the assumptions during the development of the mathematical model of the process, imposes restrictions on it. Incorrect assumptions can lead to a divergence of the

results with a real data or to gross errors, which are not acceptable in the development of equipment design.

The correct and perhaps the only solution of the problem of increasing the accuracy of the mathematical model is to check the estimates during the experimental research and the introduction of an empirical correction coefficients in to the model.

Notation

T – the temperature, K; τ – time, min; c – heat capacity, J/(kg·K); ρ – density, kg/m³; λ – coefficient of thermal conductivity, W/(m·K); q – specific thermal energy, J/kg; α – the heat transfer coefficient, W/(m²·K); r – latent heat of vaporization, J/kg; W – the moisture content of the material, %; f – a specific surface area in m²/m³; k_p – molar transfer coefficient, c; P – pressure, Pa; m – mass of a substance per unit volume, kg/m³; k – rate constant of a chemical reaction, c⁻¹; γ – the proportion of the component, %; V – velocity, m/s; ε – porosity, m³/m³; η – the degree of pyrolysis, %; e – the coefficient of blackbody radiation, W/(m²·K⁴); C – concentration of substance, mol/m³; i – the component (substance); j – water mass flow, kg/(m²·s); F – surface area, m²; A – calculated ratio; V – volume, m³; S – mass formation, kg/(m³·s); μ – the dynamic viscosity of the gas, Pa·c; B_g – the gas permeability of the particle, m²; L – length, m; σ – Stefan-Boltzmann constant (5.67·10⁻⁸ W/m²·K⁴); d – diameter, m; M – molar mass, g/mol; R – universal gas constant, J/(mol·K); X – flow of matter, mol/s; ω – the velocity of chemical reaction, mol/(s·m³); ΔH – the change in enthalpy of the system, J/mol; K – heat transfer coefficient W/(m²·K); S_x – cooling surface area, m²; β – mass transfer coefficient, kg/(m²·s); S_k – the surface of the catalyst bed, m²/m³.

Subscripts

part – particle; ef – effective; g – gas; evap – evaporation; pr – primary; 0 – the initial; w – wood; i.c. – intermediate compound; coal – coal; sol – solid phase; voi – voids; por – pores; gs – the gas stream; z – the number of reactions; rz – reaction zone; ca – cooling agent; sur – surface; cat – catalyst; atm – atmosphere;

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