Experimental study of kukersite oil shale pyrolysis by solid heat carrier

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ABSTRACT

The investigation of oil shale pyrolysis in the experimental retorting system by solid heat carrier (silica sand) was conducted. Modeling of the heat and mass transfer processes in the retorting system was performed with use of simplified mathematical model. It was shown that the radiation heat exchange plays the main role in the heat transfer between oil shale particles and solid heat carrier under the conditions of volatiles release. The maximum yield of the shale oil amounts to 73% at temperature of experiment of 560 °C, which exceeds the data obtained in the Fisher assay on 20%. The conditions that lead to increase in maximum yield of shale oil in the industrial UTT units with the rotary drum reactor were ascertained. They are mainly associated with a decrease in the solid heat carrier (ash) temperature, which leads to the inhibition of secondary reactions between ash and the acidic compounds of the shale oil.

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1. Introduction

The continuous growth in energy use in the world results in the exhaustion of traditional energy resources such as oil, gas, and coal. Therefore, the retrieval of alternative energy sources has a great importance at the present. One these sources can be oil shale primarily due to the enormous reserves and the valuable chemical composition [1]. Oil shale has a high content of mineral material that is closely integrated with organic matter (kerogen) [2]. And that is why its direct combustion in boilers is faced with some technical difficulties [3]. The oil shale kerogen contains a large amount of hydrogen. The mass ratio C/H is approximately equal to eight, which is close to the corresponding ratio for raw oil [4]. Therefore, pyrolysis or retorting of oil shale makes it possible to process up to 90% of kerogen into vapor products, which are raw materials for the production of boiler and motor fuels [5] as well as of valuable chemicals [6].

The oil shale retorting has a long history, and different technologies were developed [7]. The most advanced retorting technology is the Galoter one, the commercial realization of which put into practice in the industrial units UTT-3000 with a capacity of 3000 t of shale per day [8]. This technology is based on the oil shale pyrolysis in the horizontal rotary drum reactor at temperature of the order of 500 °C. The oil shale ash is used as a solid heat carrier. The semi-coke particles after the reactor are transported into aerated fountain furnace, where their combustion occurs at temperatures 750-850 °C, thus providing the necessary temperature of ash for subsequent heating of oil shale in the pyrolysis reactor.

A large number of investigations that aim to study the influence of main parameters of oil shale pyrolysis on the process efficiency have been conducted over the recent years. They examine the effect of retorting temperature on the products yield [9], the heat transfer characteristics of oil shale particles [10], the pyrolysis kinetics [11–13], etc. To better understand the pyrolysis mechanism as applied to the Galoter technology, the numerical analysis of the oil shale pyrolysis in rotary drum reactor was performed [14]. The developed model includes such processes as the motion of solids in the reactor, the heat transfer between solid heat carrier and fuel particles, the kinetics of kerogen decomposition, etc. The theoretical description of these processes requires some simplifications and concretization of the model parameters, which can be received on the base of experimental investigations. The main objective of this study is to clarify the specific features of heat transfer between oil shale particles and solid heat carrier under the conditions of volatiles release as well as the identifi cation of conditions that lead to maximum yield of shale oil.

2. Experimental

2.1. Materials

Oil shale samples used for experiments were obtained from Leningradsky deposit of the kukersite oil shale, Russia. These samples were crushed and sieved to three fractions with mean grain sizes of 0.35, 1.5, and 4.0 mm, respectively. After crushing and drying at room temperature to constant weight, oil shale was kept in hermetic volume.
A representative sample of oil shale was investigated by standard methods. Table 1 shows the results of proximate and ultimate analysis of the tested oil shale. The mineral part of the kukersite consists mainly of limestone (of the order of 45 wt.%). The Fisher assay yields are as follows (wt.%, dry basis): shale oil – 20.50; pyrogenic water – 2.06; coke residue – 72.03; gas and loses – 5.41. The inert particulate material (silica sand) with a mean grain size of 0.2 mm was used in experiments as the solid heat carrier.

2.2. Experimental system

During the first stage of the work, the investigation of oil shale processing with solid heat carrier using experimental retorting system was conducted. The scheme of the retorting system is shown in Fig. 1. The main element of the system is the hermetic steel retort with mixing device 1, which is placed in the shaft furnace 2, where the heating of the solid heat carrier (silica sand) occurs. The mass ratio of oil shale and solid heat carrier in the experiments was chosen so that the final temperature of the process is in the range 450-600 °C. Upon reaching the desired temperature of the heat carrier (550-700 °C), the retort is disconnected from the external heating source and at the same time it is filled with a portion of the shale.

The uniform mixing of shale with solid heat carrier is carried out by using the vertical mixing device. The time of oil shale adding and full mixing of the materials was not specially controlled, but it was determined in the range of 5-10 s based on separately conducted measurements. As the result of the heat and mass transfer processes, the thermal decomposition of kerogen occur followed by the volatiles emission. The temperature inside the retort is stabilized approximately one-two minutes after the start of the experiment.

The upper part of retort represents a dust precipitation chamber that is connected with the condenser of heavy oil 5. After passing the condenser 3, the vapour-gas mixture enters the condenser 4 for medium-light oil, which is connected with the collector of this oil 6. The final condensation of the vapour-gas mixture occurs in the condenser 7, which is located in the thermostat with negative temperature. A non-condensable gas mixture (pyrolysis gas) is supplied from the condenser 7 to the gas meter 8 and the flow meter 9, and then to the burner 10, where it is burned. During the experiment, the temperature and pressure in the retort as well as the gas-flow rate after the condensation system were registered. After the end of the experiment, the determination of quantity of received products such as gas, oil, pyrogenic water, and semicoke was made.

During the second stage of the work, the impact of alkaline-earth metals oxides contained in the shale ash on the retorting process was estimated. The kukersite oil shale contains a significant amount of calcium oxide. Therefore, this mineral was used for investigation. The experiments were performed in the Fisher retort using mixtures of oil shale and calcium oxide in ratio of 19:1, 17:3, 7:3 and 1:1. The heating rate of the retort up to the final temperature of 520 °C did not exceed 15 °C/min.

Separately, the carbonates decomposition in the oil shale depending on the treatment temperature was examined. For this purpose, parallel samples of oil shale were placed in the muffle furnace and heated to final temperatures of 600, 800, and 950 °C. Upon reaching the set temperature, the sample is kept for 2 h and then is cooled in a desiccator. The content of carbon dioxide in received samples was determined by gravimetric method, which allowed judging the degree of carbonates destruction.

3. Model description

Modeling of the heat and mass transfer processes in the experimental retorting system was performed with use of simplified mathematical model, which includes the equation of enthalpy balance between solid heat carrier and fuel, the equation of heat conductivity describing the heating of fuel particles, and the kinetic equation of the kerogen decomposition. The kerogen behavior at high temperatures is determined by the kerogen type, heating rate, final temperature, particle size, etc. [15-16]. The decomposition process begins with kerogen conversion into a plastic state – tar (TAR), which disintegrates then into the mixture of liquid hydrocarbons (OIL) and gas (GAS).

It is assumed that the heat transfer in the layer of heat carrier that surrounds fuel particles is high, so the layer is considered as isothermal. Since the size of the fuel particles is sufficiently small, they are considered as isothermal also. The heat transfer between reactor walls and the filling is ignored. At these conditions, the enthalpy balance equation can be written as:

$$c_{hc}m(T_{hc,0} - T_{hc}) = c_1(T_f - T_{f,0}) + (1 - Y_{tar})\Delta H,$$

where $c_{hc}$ and $T_{hc}$ are the heat capacity and temperature of the heat carrier; $m = \rho_{hc}/\rho_i$ is the ratio of the flow rates of the solid heat carrier $\rho_{hc}$ and the fuel $\rho_i$; $Y_{tar}$ is the tar concentration, kg/kg of kerogen; $\Delta H$ is the heat of reaction.

Fuels particles are assumed to be spherical, and any change of the particle mass and shape during devolatilization process is not taken into account. The heat transfer equation that describes heating of fuel particles can be expressed as follows:

$$d(\rho_i v_p c_i(T_f))/dt = (h + h_{rad}) s_p (T_{hc} - T_f) - \rho_i v_p k_{tar} Y_{tar} \Delta H,$$

where $\rho_i$ is the fuel particle density; $v_p = (1/6)\pi d_i^3$ is the volume of the fuel particle with the diameter $d_i$; $s_p = \pi d_i^2$ is the surface particle; $h$ is the conductive and convective heat transfer coefficient; $h_{rad} = \sigma \varepsilon (T_{hc} + T_f) (T_{hc}^4 + T_f^4)$ is the radiation heat transfer coefficient, where $\sigma = 5.67 \times 10^{-8}$ W/(m²·K⁴) is the Stefan-Boltzmann constant, and $\varepsilon = 0.8$ is the particle emissivity; $k_{tar}$ is the rate constant of the tar decomposition. In general, the heat exchange between solid heat carrier and fuel particles is carried out by conduction, convection, and radiation [17,18]. At the conditions of intensive volatiles emission from the fuel particle, one can expect that the radiation heat transfer will be predominant.

| Table 1 |
| Analysis of the tested oil shale. |
|------|------|
| Proximate analysis (wt.%)<sup>a</sup> | Ultimate analysis (wt.%)<sup>a</sup> |
| Moisture | 1.30 | C<sup>c</sup> | 30.52 |
| Volatile matter | 46.25 | H | 2.73 |
| Ash | 47.88 | S | 0.52 |
| Fixed carbon | 4.57 | N | 0.16 |
| Lower heating value (kJ/kg) | 10,576.30 | O<sup>c</sup> | 16.89 |

<sup>a</sup> As-received basis.
<sup>b</sup> Total carbon.
<sup>c</sup> Calculated by difference.
The dynamics of tar decomposition is usually considered as a first order reaction relatively to the tar concentration $Y_{tar}$:

$$dY_{tar}(T_f)/dt = -k_{tar}(T_f)Y_{tar}(T_f).$$  \hspace{1cm} (3)

The rate constant $k_{tar}$ for kerogen of the kukersite oil shale, which was restored on the basis of the experimental data, is equal to $6.3 \times 10^{13}$ exp.$(-25,600/T_f)$ s$^{-1}$ [19]. This expression is close to data [20] for kerogens of II/I type. The thermophysical characteristics of the kukersite oil shale are equal: $c_t = 1130$ J/(kg-K); $\rho_t = 1860$ kg/m$^3$; $\Delta H = 1.46 \times 10^7$ J/(kg of dry oil shale); $c_{hc} = 840$ J/(kg-K).

The process of volatiles yield is accompanied by different secondary reactions. These reactions primarily include coking and decomposition of the shale oil. The OIL coking occurs in the interior of oil shale particles as well as on the surface of heat carrier particles with the deposition of coke (COKE) and GAS release. The OIL decomposition occurs in the free volume of the reactor and leads to formation of lighter liquid components and gas. The dynamics of secondary reactions can be described with help of corresponding rate constants [14].

4. Results and discussion

4.1. Heat transfer between heat carrier and fuel particles

One of the main objectives of this study is to establish the mechanism of heat transfer between solid heat carrier and fuel particles. Typical behavior of temperatures $T_{hc}$ and $T_f$ as a function of the process time is shown in Fig. 2, where experimental data received in this study are compared with numerical estimations. Theoretical curves were obtained as a result of the calculation according to the Eqs. (1)–(3) with the conductive and convective heat transfer coefficient $h = 0$. Good agreement between calculated and measured temperatures $T_{hc}$ suggests that the radiation heat exchange plays the main role in the heat transfer. Some differences between theoretical curve and experimental points for the temperature $T_{hc}$ can be explained by the incomplete mixing at the first stage of the process, and the mixture heating from the reactor walls at the last stage.

Fig. 2 shows also the measured data and numerical estimations on the emission rate of volatiles from the oil shale particles. On the whole, one can note a satisfactory agreement between these data. The volatiles emission at the thermal decomposition of the kerogen begins at the temperature near 300 °C [21,22]. At this stage of the process, the oxygen content of the kerogen decreases significantly with release of water vapor and carbon dioxide. The greater part of oxygen in the chemical structure of the kukersite oil shale belongs to hydroxyl and carboxyl groups (respectively, 43 and 14% of the oxygen containing structural units) [23]. These functional groups are the precursors of water vapor and carbon dioxide formation under pyrolysis. An intense release of these gas components is shown in Fig. 2 by triangles at process time $t < 20$ s. This release inhibits the conductive and convective heat exchange between solid heat carrier and fuel particles at the initial stage of the pyrolysis. The theoretical curve ($-dY_{tar}/dt$) is calculated with use of the rate constant $k_{tar}$, numerical value of which was received in [19] as a least-square fit to experimental data for shale oil release. It is seen that the shale oil emission begins at the temperature $T_f = 400$ °C.

A detailed comparison of experimental and calculated data on the change of the heat carrier temperature $T_{hc}$ depending on the process time $t$ is shown in the Figs. 3 and 4. The data in the Fig. 3 were obtained for particles with a diameter of $d = 4$ mm at various initial temperatures $T_{hc,0}$ and ratios $m = G_{hc}/G_t$ where $G_{hc}$ and $G_t$ are the flow rates of solid heat carrier and fuel, correspondingly. It is seen that all calculated curves in the final stage of the process lie below the experimental points. This fact is explained by the influence of the hot walls of the reactor, which is not included in the enthalpy balance Eq. (1). The data in the Fig. 4 were received for particles of various diameters. In this case, the agreement between the experimental and calculated data for particles of small diameter is not satisfactory. The reason for the discrepancy may lie in the fact that the rate of heating of the small fuel particles is large enough so that the temperature of the heat carrier does not have time to be equalized. The heat transfer modeling inside of the heat carrier layer requires the use of at least 2D model, and in the present case is not considered.

4.2. Thermal decomposition of kerogen

The further object of the present study is to determine the yield of the pyrolysis products in conditions that close to real ones in the rotary drum reactor of the UTT unit. Fig. 5 gives the yield of gaseous products depending on the temperature of experiment $T_{exp}$ that represents the steady temperature of the solids mixture at the final stage of the process. It can be seen that the GAS yield decreases with increasing $T_{exp}$, and then begins to rise sharply. This rise can be identified with the shale oil decomposition in the free volume of the reactor. The yield of the water vapor has the opposite tendency. It should be noted that value of this yield is sufficiently high (it reaches 20 wt.% at $T_{exp} = 500$ °C).

The yield of the COKE is shown in Fig. 6. There is a fixed downward tendency in the COKE yield with increasing temperature $T_{exp}$. The COKE yield at $T_{exp} > 550$ °C does not exceed a few percents. The kinetics of OIL coking on the surface of heat carrier particles was considered in [24].
The following expression for the reaction rate was received:

\[ mk_c y_{oil}(1 + Bk_c y_{oil}t)^{-1} \]

where \( k_c = 0.0104 \text{ m}^3/(\text{kg} \cdot \text{s}) \) is the coking rate constant, \( y_{oil} \) is the concentration of the shale oil in the gas, \( B = 215 \) is deactivation constant, and \( t \) is the process time. The liquid products of the kukersite oil shale pyrolysis are dominated by hydrocarbons and oxygenated aromatic compounds [25]. The average value of \( y_{oil} \) for this mixture at \( T_{exp} = 540 \degree \text{C} \) can be estimated as 2 kg/m\(^3\). Calculations show that the COKE yield at these conditions is almost independent of temperature \( T_{exp} \) and is equal to 8.8 wt.\%.

The greatest interest among the volatiles represents the shale oil. The experimental yield of this product is shown in Fig. 7. One can see that the OIL yield increases at temperature growth up to \( 550 \degree \text{C} \). Further reduction of this parameter is connected with the presence of secondary reactions of the OIL decomposition on lighter liquid components and gas in the free volume of the reactor. The decomposition process can be considered as a first order reaction relatively to the OIL concentration with the rate constant \( k_{oil} \) that is equal to \( 1.7 \times 10^{10} \exp\left(-\frac{20,480}{T_{exp}}\right) \text{ s}^{-1} \) for the kukersite oil shale [19]. Numerical estimations with use of this rate constant show that the decrease of the OIL concentration at \( T_{exp} = 580 \degree \text{C} \) reaches 20%, which is in good agreement with the experimental data presented in Fig. 7.

The increase of the OIL yield is an important task in the way of improving the efficiency of the UTT units. In this connection, it is interesting to compare the values of this process parameter for different process conditions as applied to the kukersite oil shale pyrolysis. Fig. 8 shows the OIL yields as a function of retorting temperature \( T_{exp} \) as applied to: (1) flash pyrolysis of fine-grained oil shale particles (<100 \( \mu \text{m} \) in size) heated by the gaseous heat carrier with rates of the order of \( 10^3 \)–\( 10^5 \degree \text{C}/\text{s} \) [19]; (2) pyrolysis of small oil shale particles (0.35–4.0 mm) in the retorting system with solid heat carrier that ensures the heating rate of the order of \( 10^3 \degree \text{C}/\text{min} \) (this study); (3) pyrolysis of the kukersite oil shale in the pilot unit UTT-500 [26].

In the first case, the OIL yield reaches maximum value of the order of 80% at \( T_{exp} = 600 \degree \text{C} \). High heating rates are achieved by using fine particles, which leads to the high heat transfer between particles and the gaseous heat carrier. The further increase in temperature \( T_{exp} \) leads to the OIL decomposition [19]. The concentration of pyrogenic water in the pyrolysis products is not exceeding a few percents. This distinguishes the fast pyrolysis data from the data of this study. Probably, the higher heating rate of the oil shale particles promotes a separation of large molecular fragments instead of separation and subsequent stabilization of hydroxyl groups that are the precursors of the water molecules formation.

In the second case (this study), the maximum OIL yield amounts to 73% at \( T_{exp} = 560 \degree \text{C} \), which exceeds the data obtained in the Fisher assay on 20%. The high heating rate in this case is achieved by the efficient mixing of the materials by the stirring device. This device is able to provide a complete homogeneity of the mixture in a short time, and, respectively, the uniformity of heating of oil shale particles.

The data obtained at the pilot unit UTT-500 (the third case) are characterized by the lowest maximum value of the OIL yield. The heat transfer between the heat carrier and oil shale essentially depends on the mixing of materials, which occurs less efficient in the rotary drum.
reactor of the UTT unit. It is likely that a portion of the oil shale entering the reactor is in contact with the solid heat carrier, which leads to overheating of this portion. Another part of the oil shale is heated by the already hot oil shale particles (semicoke), and by heat carrier particles, which have a reduced temperature. In addition, the OIL yield decrease in this case may be associated with the use of the oil shale ash as the heat carrier, which can contribute to the appearance of the secondary reactions (see below).

4.3. Interaction of shale oil with oxides of alkaline earth metals

As was mentioned above, the Galoter technology is based on the use of oil shale ash as the solid heat carrier [14]. The semicoke particles that are formed in the pyrolysis reactor are burned up in the aerated fountain furnace at the temperature 750-850 °C. The resulting heat is used to warm the heat carrier, which is then separated from the stream of ash and flue gases and returned to the pyrolysis reactor. The simplified scheme of the process is given in Fig. 9. As a result of heat treatment in the furnace, the organic mass of the semicoke particles is almost completely oxidized. Simultaneously, the carbonate compounds contained in the mineral mass dissociate [27]. At this, the higher temperature in the furnace causes more complete decomposition of the carbonates. The dependence of the degree of dissociation of carbonates on the temperature is shown in Fig. 10. The released carbon dioxide is mixed with the flue gases and removed from the reaction zone. Accordingly, the residuary solid phase contains oxides of alkaline earth metals MeO (in the main CaO and MgO).

The separation of oxides of alkaline earth metals from the solid heat carrier is a complex task that is not realizable at the UTT units. Therefore, the oxides are returned in the pyrolysis reactor, where they contact with the products of the kerogen thermal decomposition. The spectroscopic and pyrolytic techniques indicate the presence of a large number of carboxylic acids and oxygenated aromatic compounds (3-n-alkylphenols and 5-n-alkyl-1,3-benzenediols) in the liquid products of the kukersite oil shale pyrolysis [28]. The interaction of these compounds with oxides of alkaline earth metals leads to their absorption. In particular, the reactions of CaO with phenols and carboxylic acids can be written as:

\[ \text{CaO} + 2 \text{RC}_6\text{H}_4\text{OH} \rightarrow (\text{RC}_6\text{H}_4\text{O})_2\text{Ca} + \text{H}_2\text{O}, \]

\[ \text{CaO} + 2 \text{RCOOH} \rightarrow (\text{RCOO})_2\text{Ca} + \text{H}_2\text{O}. \]

The phenolates and salts of alkaline earth metals formed in this process are accumulated on the semicoke and ash particles and then are transferred to the aerated fountain furnace. As investigations show, the semicoke of the UTT-500 unit contains 1.3-1.5 wt.% of the acidic organic compounds that are extracted with sodium hydroxide solution [27]. The chemical analysis of the extract indicates the presence in the main of phenolates and salts of carboxylic acids. Recent experimental data [29] show that the acidic compounds yield during the pyrolysis with abundant addition of CaO is significantly reduced.

It should be noted that the influence of the mineral matrix on the shale oil yield is complex. As investigations show, the pyrolysis reactions are catalyzed by alkaline earth metal cations in carbonates and inhibited by silicates [30,31]. The catalytic effect of the carbonates for Huadian oil shale seems to be greater than the inhibition one [32]. In addition, the adsorption of heavy hydrocarbon products of the kerogen pyrolysis occurs on the mineral surfaces, which leads to the cracking of the trapped hydrocarbons [33]. The objective of the present study is the investigation of the chemisorption of acidic products of the oil shale decomposition on CaO particles.

In order to evaluate the effect of CaO on the reduction of the shale oil concentration, a series of experiments in the Fischer retort has been conducted in this study. The results of measurements are shown in Fig. 11. It is seen that the oil concentration decreases up to 20 wt.% with increase of CaO content in its mixture with the oil shale. The effect of the additive is not changed with further increase in the concentration of CaO. A direct consequence of the oil concentration decrease is a corresponding increase in the concentration of organic matter of semicoke.

![Fig. 9. Simplified scheme of the Galoter process.](image-url)
The decrease of gas concentration is explained by absorption of CO₂ on the CaO particles.

The equilibrium dissociation temperature of MgCO₃ and CaCO₃ at CO₂ partial pressure \( P_{\text{CO}_2} = 0.2 \text{ atm} \) is equal approximately 570 and 780 °C, correspondingly. This means that the reaction will go towards the formation of carbonates at the temperature in the aerated furnace. The mineral part of the kukersite oil shale contains of the order of 45 wt.% of CaO. On the other hand, the MgO concentration is not exceeding a few percents. The realization of the semicoke burning in the furnace at a temperature below 780 °C is sufficiently simple. The temperature reduction can be achieved by a decrease of the air flow that is needed for combustion and fluidization. This will increase the residence time of the semicoke particles in the furnace, which reduces the combustible losses and compensates the opposite kinetic effect due to lower temperature in the furnace. It must be pointed that the partial pressure of CO₂ in the furnace will increase with decreasing excess air ratio. The increase of CO₂ partial pressure will shift the equilibrium of CaCO₃ decomposition reaction to higher temperatures. This means that one can almost completely suppress the dissociation of carbonates by lowering the furnace temperature, and thereby avoid the presence of oxides of alkaline earth metals in the solid heat carrier.

5. Conclusions

One of the main objectives of this study is to clarify the specific features of heat transfer between oil shale particles and solid heat carrier under the conditions of volatiles release. The comparison of the received experimental data with the results of numerical calculations showed that the radiation heat exchange plays the main role in the heat transfer.

The maximum shale oil yield in experiments amounts to 73% at the temperature \( T_{\text{exp}} = 560 \degree \text{C} \), which exceeds the data obtained in the Fisher assay on 20%. The sufficiently high heating rate is achieved by the efficient mixing of the materials by the stirring device. The comparison of the received experimental data with data of flash pyrolysis of fine-grained oil shale particles heated by the gaseous heat carrier showed that the flash heating rate of the oil shale particles promotes a separation of large molecular fragments instead of separation and subsequent stabilization of hydroxyl groups that are the precursors of the water molecules formation. The data obtained at the pilot unit UTT-500 are characterized by the lowest maximum value of the shale oil yield.

The shale oil yield decrease in the case of the pilot unit UTT-500 may be associated with the use of the oil shale ash as the heat carrier, which can contribute to the appearance of the secondary reactions. The mineral part of the kukersite oil shale contains of the order of 45 wt.% of CaO. In order to evaluate the effect of CaO on the reduction of the shale oil concentration, a series of experiments in the Fischer retort has been conducted. The results of measurements showed that the oil yield decreases up to 20 wt.% with increase of CaO content in its mixture with the oil shale. It is recommended to reduce the furnace temperature at the expense of the decrease of the excess air, which reduces the amount of oxides of alkaline earth metals in the solid heat carrier and thus inhibits the secondary reactions in the pyrolysis reactor.

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Fig. 11. The yield of pyrolysis products in the Fisher assay as a function of CaO concentration.


