Combustion and Processing of Rice Husk in the Vibrofluidized Bed of Catalyst or Inert Material

A. D. SIMONOV, T. I. MISHENKO, N. A. YAZYKOV and V. N. PARMON

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,
Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

E-mail: A. D. Simonov@catalysis.nsk.su

Abstract

In the present work, some data on catalytic combustion of one of the most widespread vegetative remainders − rice husk are adduced. The rice husk is used not only as a fuel, but also as a source of silicon for semiconductor industry, the synthesis of silicon carbides and silicon nitrides, *etc*. We studied the rice husk oxidation in the vibrofluidized bed of either a catalyst or an inert material in conditions allowing to reproduce with an adequate accuracy the data on scraps combustion in the dense and unloaded phase of the fluidized bed. It is found that the process of the rice husk combustion is localized completely in the bed of the catalyst. In the bed of an inert material the process occurs in a space above the bed; consequently, exhausts contain a fair quantity of CO. Studies on solid products of the rice husk combustion have shown that their texture is determined mainly by silica, which is contained in rice husk as amorphous silica $SiO_2 \cdot nH_2O$. The adsorption ability of these solid products in respect to methylene blue (MB) is investigated. With increasing the process temperature, the value of limiting MB adsorption by the solid products passes through a maximum at the process temperature 600 °C. It is found that the values of the limiting MB adsorption for the solid combustion products in the bed of the catalyst exceed those for solid products obtained in the bed of an inert material. Under discussion are also some distinctions of the process of rice husk processing in the vibrofluidized beds of either catalyst or inert material.

INTRODUCTION

Biomass is the most ancient source of energy for humans. Till now wood fuel remains the main energy source in many countries of the world [1]. Important sources of biomass are now also vegetative remainders (wheat and corn straw, chaff, rice and oat husk, *etc*.). The traditional combustion of biomass in a torch furnace at 1200−1600 °C for power purposes has an essential disadvantage due to high emission of toxic substances with exhaust gases (CO, nitrogen and sulfur oxides, benzpyrenes and other).

In the fluidized bed of inert particles, the process of solid organics combustion is essentially intensified in comparison with combustion of those in a fuel-bed furnace due to more vigorous transport of air oxygen to solid fuel particles [2]. A capability to burn the pulverized solid fuel in the fluidized bed makes this process similar to the torch burning with an advantage that it is possible to regulate the residence time of the fuel particles in the bed and to achieve a high burn-off of the fuel at rather low temperatures of the bed, 850−1000 °C. However, in this case the concentration of the toxic substances in the exhaust gases also remains high enough.

A technology of the fuel combustion in the fluidized bed of catalyst, which was developed by the Boreskov Institute of Catalysis on an industrial scale [3, 4], avoids many disadvantages of the conventional high temperature combustion of the fuel. The technology is based on a combination of four principles: use of heterogeneous catalysts for the complete oxidation of combustibles; combustion of fuels in the fluidized bed of the catalyst particles; combustion of the fuel without a signifi-

cant excess of air; coupling the processes of heat generation and removal within the same fluidized bed.

The catalytic combustion differs essentially from the burning in traditional understanding, since the fuel is oxidized on the surface of solid catalysts without a flame formation [5]. The catalyst action during the complete oxidation (or heterogeneous burning) of the fuel-air mixes is based on the interaction of fuel components with superficial oxygen of the catalyst with the sequential regeneration of the restored surface of the catalyst by oxygen from the gas phase. Depending on the catalyst activity, the process of complete oxidation of many combustibles can proceed even at 250−300 °C. Compared with the known combustion methods, the catalytic combustion allows:

− to decrease the temperature of organic fuel combustion from 1200−1600 °C to 300−700 °C;

− to mitigate requirements for thermochemical stability of furnace construction materials and reduce an erosion of apparatus;

− to diminish heat losses through the apparatus wall;

− to improve explosion safety of the heat generating installations;

− to reach high (up to $5 \cdot 10^8$ kJ/(m^3 h)) values of the power loading during the fuel oxidation with a significant decrease of the size, weight and metal consumption of the installations;

− to exclude secondary reactions which form toxic products.

Basing on the new technology a variety of apparatuses has been designed for the heating and evaporation of liquids, materials drying and heating, detoxification of industrial gaseous, liquid, and solid wastes, and so on.

In this work, we present some experimental data on the catalytic combustion of one of the most widespread vegetative remainders − rice husk (RH). The RH is widely available in many southern countries and used now not only as a fuel, but also as a source of silicon for semiconductor industry, the synthesis of silicon carbide and silicon nitride, *etc.* [6]. We studied the RH oxidation in the vibrofluidized bed of both a catalyst and an inert material in conditions allowing to reproduce with an ade-

TABLE 1

Some chemical characteristics of the rice husk under investigation

Components	Concentration, % mass*
General analysis	
Volatile substances	70.2
Fixed carbon	14.1
Ash	15.7
Elemental analysis	
C	43.5
H	5.5
O	35.2
N	0.05
S	0.02
Cl	0.01
Ash	15.7

*On dry substance.

quate accuracy the data on scraps combustion in the bubble and emulsion phase of the fluidized bed.

EXPERIMENTAL

In this work we used the rice husk from Vietnam. Table 1 shows the chemical composition of RH under investigation.

The scheme of the laboratory-scale plant for the RH combustion in the vibrofluidized bed of the catalyst or an inert material is presented in Fig. 1. The reactor *1* was a stainless steel cylinder 23 mm in diameter and 100 mm in height. The bottom of the reactor was made of a stainless steel net with sell of 0.5 mm. The reactor was loaded either by an inert material (river sand) or catalyst (16.6 cm^3 each) with the particles of 1.5−2.0 mm in diameter. Then electric heater *2* and vibrator *5* were turned on. The frequency of the reactor oscillations was 50 Hz, the vibrational amplitude was 1 mm. The temperature in the reactor was controlled with a thermocouple. As the reactor temperature achieves the operation level, the crushed RH particles (0.2−0.4 mm) were fed with the supply rate 4.6 g/h. The total supply of air into the reactor and to a husk feeder *8* made up 55 l/h. The outlet gas mixture was cooled in a heat exchanger *4*. Further, the solid combus-
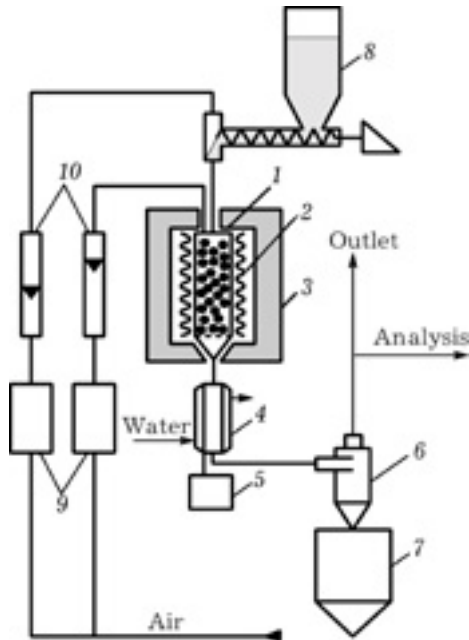
Fig. 1. The scheme of the laboratory-scale plant for the RH combustion in the vibrofluidized bed of the catalyst or an inert material: 1 − reactor, 2 − electric heater, 3 − heat isolation, 4 − heat exchanger, 5 − vibrator, 6 − cyclone, 7 − tank for ash, 8 − screw feeder with tank, 9 − air flow regulators, 10 − rotameters.

tion products were separated in a cyclone 6 and collected in a bunker 7.

The concentrations of CO, CO_2, CH_4, H_2, SO_2, and O_2 in the flue gas were determined using the gas chromatography method. A commercial $CuCr_2O_4/\gamma\text{-}Al_2O_3$ (IC-12-70) catalyst with 15 % mass of the active component was used for the experiments.

The initial RH humidity was determined by weighting the samples after their drying at 120 °C for 4 h. The quantity of volatile substances in the RH was determined by weighting the dried samples after their heating at 850 °C for 7 min. The content of ash, organic part in initial RH and products of the RH combustion was determined by weighting the samples after their calcination at 800 °C in air for 2 h. The burn-off of the RH was calculated with the formula:

$$\beta = (A_S - A_0)/A_S (1 - A_0)$$

where A_0 is the ash fraction in the initial dried RH sample, while A_S is the ash fraction in the solid combustion products.

The composition of the mineral part of the initial RH was determined using an VRA-20

X-ray fluorimeter (Germany) equipped with a fluorescent analyzer. The morphological analysis of the initial RH and products of the RH combustion was conducted with an auto-emission high-vacuum raster electronic microscope BS-350 (Czechoslovakia).

The "bleaching" adsorption from water ability of the RH processing products was determined with the methylene blue (MB) adsorption [7]. A commertial activated birch coal was used for comparison.

RESULTS

Combustion of rice husk

The RH under investigation contained 15.7 % ash, 14.1 % fixed carbon and 70.0 % volatile substances (see Table 1). The RH ash consisted of 94 % silica and also 2.5 % potassium, 0.6 % calcium, 0.4 % magnesium, and 0.2 % manganese. The content of sodium, aluminum, iron, phosphorus and sulfur in the ash was less than 0.1 % mass.

Figure 2 shows the dependence of the RH burn-off on the vibrofluidized bed temperature. The RH burn-off increases by 5−10 % with the rise in the temperature from 500 to 700 °C in both the bed of the catalyst and the
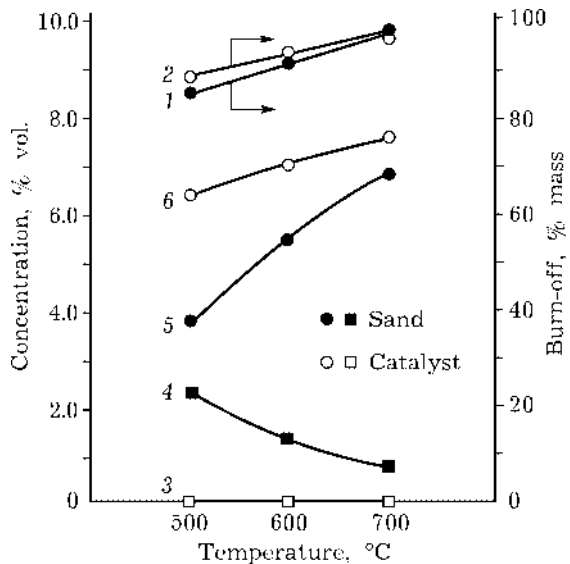

Fig. 2. The RH burn-off (1, 2) and concentrations of CO (3, 4) and CO_2 (5, 6) in the flue gas vs. the temperature of the rice husk combustion in the vibrofluidized beds of the catalyst and inert material (sand), respectively.

bed of sand. It is seen that the difference in the RH burn-out values for the catalyst and sand beds is unsignificant.

Much more significant is change of the CO and CO_2 concentrations in the flue gas (see also Fig. 2). CO in the flue gas after the catalyst bed is practically absent in the entire temperature range from 500 to 700 °C, *i. e.*, the combustion of both volatile compounds and CO is completely localized in the bed of the catalyst. On the contrary, in the bed of the sand, the combustion appears to be not finished, and the flue gas contains a fair quantity of CO, the CO concentration exceeding 0.5 % vol. even at 700 °C.

Structural, textural and adsorption characteristics of solid products of the RH combustion

Of a top practical interest seem to be characteristics of the ash (*i. e.*, solid products) of the RH combustion.

A typical texture of the RH ash external surface, according to SEM, is shown in Fig. 3, *a*. Solid products of the RH combustion in the vibrofluidized catalyst or sand bed at 500−700 °C have similar texture due to high contents of silica in the RH external epidermis [6]. A lateral chip of an ash particle, obtained at the RH combustion in the vibrofluidized bed of the catalyst at 700 °C, is shown in Fig. 3, *b*. Together with the well saved structure of the external epidermis (*1*), the structure of the RH internal layers (tubular (*2*) and spongy (*3*) parenchyma), which contain small quantity of silica, is also kept safe.

The X-ray diffraction analysis showed that both initial RH and the solid RH combustion products in the catalyst bed at 500−700 °C have no crystalline phases. The solid products, obtained at the RH combustion in the sand bed at 500 °C, have no crystalline phases too. However, in the solid products, obtained at the RH combustion in the sand bed at 600−700 °C, α-tridymite and α-cristobalite crystalline phases of silica are detected.

Some texture and adsorption characteristics of solid products, obtained at different temperatures of the RH combustion, are given in Table 2. With the process temperature rise from 500 to 700 °C, the specific surface of the solid products, which are obtained in the catalyst
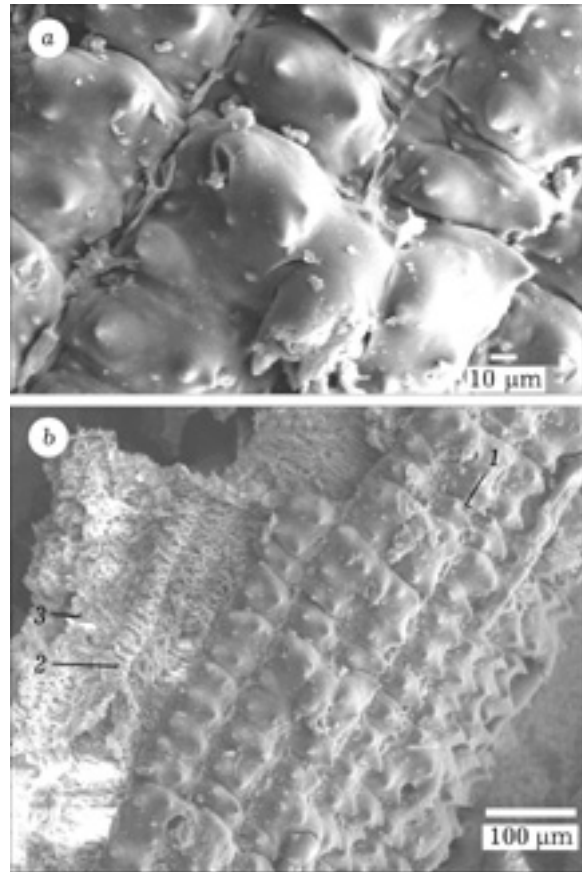

Fig. 3. Scanning electron micrographs (SEM) of the rise husk after its treatment in the vibrofluidized bed of either the catalyst or sand at 700 °C: *a* − outer surface of rise husk ash; *b* − lateral chip of the ash particle (*1* − epidermis; *2* − tubular parenchyma; *3* − spondy parenchyma).

bed, increases in value. In the case of the sand bed, the temperature rise from 500 to 600 °C leads to an increase of the specific surface, while at 700 °C its value sharply decreases. The total pore volume of the solid products (see Table 2) varies in the same way. The values of the specific surface and total pore volume of the solid products, obtained at the RH combustion in the catalyst bed, exceed considerably the corresponding values for the products, obtained in the bed of the sand.

Table 2 shows also the adsorption ability of the solid products of the RH combustion in respect to methylene blue. With increasing the RH combustion temperature, the value of the limiting MB adsorption passes through a maximum at the process temperature 600 °C in both cases. However, the values of the MB adsorption for the solid products, obtained in the catalyst bed, exceed those for the products,

TABLE 2

Some texture and adsorption characteristics of the solid products of the rice husk combustion and a commercial activated coal

Temperature, °C	Specific surface, m^2/g		Pore volume, cm^3/g		Adsorption of MB, mg/g	
	Sand	IC-12-70	Sand	IC-12-70	Sand	IC-12-70
120*	1.1		0.005		–	–
500	126	160	0.13	0.15	20.0	42.5
600	156	189	0.15	0.17	42.5	52.5
700	124	207	0.15	0.18	25.0	47.5
900**	730		0.49		137.5	

*Initial rice husk after drying.
**A commercial birch activated coal.

obtained in the bed of the sand, by a factor of 1.5−2.0. Note that this value is only 2.5 times less than the value of the MB adsorption for an industrial activated coal (Table 3).

DISCUSSION

An important feature of free fluidized bed of solid particles is its non-uniformity in the volume and time. Inside the bed, one can distinguish two phases, which are subsequently replacing each other: there are gas bubbles and clusters of the bed particles (or the so-called emulsion phase). The mass transfer between the emulsion phase and bubble occurs through the external boundary of the bubble. The main quantity of the gas, which exceeds quantity necessary for the fluidization, passes through the bed as the bubbles [8]. However, the filtration of the gas through the emulsion phase is also significant. In the case of the fluidization of large particles with diameter more than 1.5 mm, the value of the filtration flow achieves

TABLE 3

The experimentally measured temperature of particles of active sludge during their combustion in the beds of a catalyst and sand (according to [13,14])

Temperature of the bed, °C	Temperature of particles of active sludge, °C	
	Catalyst	Sand
500	500	540
600	600	750
700	730	900

45 % over the quantity of the gas necessary for the fluidization [2].

The particles of solid fuel with the size being equal to or exceeding the size of inert particles of the fluidized bed, burn out predominantly in the emulsion phase. The small-size particles burn out in the emulsion phase as well as in the bubbles. The porosity of the vibrofluidized bed depends on the vibration conditions. At the top-to-down filtration of the mixture of air and solid fuel small-size particles, the vibrofluidized bed remains homogeneous. Therefore, the data obtained in the present work for the RH combustion in the vibrofluidized bed of an inert material or catalyst reproduce precisely enough the process of the RH combustion in the fluidized bed of the same material.

Generally, in the vibrofluidized or fluidized bed of inert particles, the combustion of solid fuels proceeds in three stages [9]: (1) initial heating of the fuel particles, which stimulated the emission of volatile substances and the coke formation; (2) combustion of these volatile substances in the gas phase; (3) combustion of the coke. At the combustion of large fuel particles, the emission of the volatile substances occurs mainly before the ignition of the coke and the substances burn out in the gas phase, with heating and activating the particles of the coke. The heated particles of the coke promote the combustion of volatile substances. On the other hand, the emission of the volatile substances retards transport of oxygen to the coke surface. Therefore, the coke combustion proceeds only after the burning-

out of the volatile substances, with the temperature of burning particles being by 100–300 °C higher than the temperature of the fluidized bed of an inert material [9–11].

In the case of the combustion of small-size RH particles, the coke ignition occurs before the completing emission of the volatile substances, and thus the burning of the coke and volatile substances proceeds at the same time. The burning-out of volatile substances is not completed in the bed of inert material; for this reason the exhaust gases contain a significant quantity of CO (see Fig. 2). However, in this case a flame shell around the RH particles also forms. As a result, the temperature of the burning RH particles exceeds considerably the temperature of the vibrofluidized bed bulk. It is easy confirmed by visual observations as well as by the presence of α-tridymite and α-cristobalite crystalline phases in the solid products of the RH combustion at 600–700 °C, since the formation of α-tridymite and α-cristobalite crystalline phases is possible only at temperatures above 900–1000 °C [12].

The replacement of inert particles in the vibrofluidized bed by the catalyst particles does not change the general scheme of the RH combustion. However, in this case, the evolving volatile substances are oxidized mainly on the catalyst surface, for example, according to the scheme:

$$CO + [O] = CO_2 + [\ ] \tag{1}$$

$$O_2 + 2[\ ] = 2[O] \tag{2}$$

where [ ] stands for an oxygen vacancy on the catalyst surface; [O] is surface oxygen of the catalyst.

The catalytic oxidation of CO and volatile substances results in an increase of the oxygen concentration near the RH particles and increases their burn-off. At the same time, the temperature of the oxidized RH particles does not exceed the temperature of the vibrofluidized catalyst bed, and thus a flame shell round the burning particles does not form. It is also confirmed by visual observations and by the absence of any silica crystalline phase in the ash. The same phenomenon was observed previously at the combustion of active sludge in the fluidized catalyst bed [13, 14], where the

flame shell does not form and the temperature of the sludge particle was practically equal to the temperature of the bed (see Table 3). This experiment was carried out with placing the active sludge globules of 5–8 mm in diameter in the fluidized bed of the sand or catalyst, a thermocouple being set in each granule. The temperature was fixed during the burning-out of granule.

At 500 °C, the burn-off of RH achieves 85–90 % in the bed of the catalyst as well as in the bed of an inert material (see Fig. 2). It means that practically all volatile substances and the main part of fixed carbon (see Table 1) burn out at 500 °C. At the consequent increase of the combustion temperature up to 700 °C, the burn-off increases only by 5–10 % (see Fig. 2). It is known [2, 8–11] that heterogeneous combustion of the coke carbon is the most long stage, which limits the overall process of the solid organic substances combustion. The interaction of carbon and oxygen is determined by summary reactions:

$$C + O_2 = CO_2 \tag{3}$$

$$2C + O_2 = 2CO \tag{4}$$

$$CO_2 + C = 2CO \tag{5}$$

$$2CO + O_2 = 2CO_2 \tag{6}$$

The last reaction (6) in the absence of water proceeds with a noticeable speed at temperatures above 700 °C. In the presence of water, CO is oxidized according to a free radical mechanism under lower temperatures. The oxidation of carbon with carbon dioxide, according to thermodynamic equilibrium of reaction (5), is possible only at temperatures above 600 °C [15].

The rate of the coke combustion depends on both the kinetic factors of the interaction of carbon with O_2 and CO_2 and the transport of oxygen to the carbon surface through a boundary gas layer around the burning particle [16].

It is widely accepted that the process of the coke combustion in the fluidized bed of inert material is restricted by the diffusion of oxygen to the coke surface [2, 8–11]. In the low temperature region (below 800–900 °C), the combustion proceeds according to reactions

(3) and (4). CO forms in reaction (4), is oxidized in the coke boundary layer and also reduces the concentration of oxygen at the coke surface. In addition, the particles of the inert material in the emulsion phase of the fluidized bed enclose coke particles. This enclosing leads to slowing down of the oxygen transport to the carbon surface. The ash shell, which forms around the coke particles during the carbon burning, also leads to slowing down the oxygen supply to the carbon [17].

As mentioned above, in the fluidized bed of inert material, the temperature of the burning carbon particles is by 100−300 °C higher than the temperature of the bed bulk. Consequently, if the temperature of the bed is 600−700 °C, the carbon particles are heating up to 900−1000 °C, and the combustion of carbon according to the reaction (5) is possible. It results in an increase of the CO concentration in the boundary layer near the coke particles and a decrease in the oxygen concentration on the coke surface at the CO oxidation according to the reaction (6).

In the presence of the catalyst, the coke combustion in the temperature range 500−700 °C proceeds via reactions (3) and (4). However, in this case, the catalyst makes a significant contribution to reaction (6) as provided by schemes (1) and (2). This results in an increase of the oxygen concentration in the boundary gas layer around the coke particles. Though the temperature of coke particles in the vibrofluidized bed of an inert material is close to those for the catalyst bed (see Table 3), the coke burn-off in the catalyst bed appears to be slightly greater or equal to the coke burn-off for the inert material bed. This seems to result from increasing the oxygen concentration in the boundary layer around the burning coke in the catalyst presence (see Fig. 2).

CONCLUSION

Thus, the presence of the catalyst provides a sufficiently high burn-off of the RH at the same temperature of the vibrofluidized bed and the RH particles. This process appears to be environmentally benign, since in the flue gas after such combustion there are no products of partial oxidation of organics like CO even at rather low bed temperature, 500 °C. Of importance is also that the process enables to obtain in one stage, *i. e.*, without additional stage of the coke activation, some valuable solid products with a high specific surface and good adsorption properties. Indeed, such solid product can be of large practical interest for the rice-growing countries.

REFERENCES

1 S. S. Sofer, O. R. Zaborsky, Biomass Conversion Process for Energy and Fuels, Plenum Press, New York−London, 1981.
2 J. G. Yates. Fundamentals of Fluidized-Bed Chemical Processes, Butterworths, London, 1983.
3 A. D. Simonov, N. A. Yazykov, P. I. Vedyakin *et al.*, *Catal. Today*, 60 (2000) 139.
4 Pat. 826798 Russia, 1983.
5 G. K. Boreskov, Heterogeneous Catalysis, Nauka, Moscow, 1986 (in Russian).
6 D. F. Houston, Rice and its Quality, Kolos, Moscow, 1976, pp. 271−304 (in Russian).
7 D. A. Kolyshkin, K. K. Michailova, Active Coals, Khimiya, Leningrad, 1972 (in Russian).
8 J. F. Davidson, D. Harrison, Fluidization, Acad. Press, London, 1971.
9 V. A. Borodulya, L. M. Vinogradov, Combustion of Solid Fuel in Fluidized-Bed, Science and Engineering, Minsk, 1980 (in Russian).
10 I. B. Ross, M. S. Patel, J. F. Davidson, *Trans. J. Chem. Engrs.*, 59 (1981) 83.
11 M. Radovanovich, Combustion of Fuel in Fluidized-Bed, Energoatomizdat, Moscow, 1990 (in Russian).
12 N. M. Bobkova, Physical Chemistry of Silicates, Vysshaya Shkola, Minsk, 1977 (in Russian).
13 A. D. Simonov, N. A. Yazykov, E. I. Yepifantseva *et al.*, *Chemistry for Sustainable Development*, 1 (1993) 289.
14 A. D. Simonov, N. A. Yazykov, *Chemical Industry*, 3 (1996) 47.
15 P. D. Woker, F Rusinko, L. G. Austin, *Adv. Catal.*, 11 (1959) 133.
16 B. V. Kantorovich, Fundamentals of the Theory of Combustion and Gasification of Solid Fuel, Akademiya Nauk SSSR, Moscow, 1958 (in Russian).
17 V. V. Pomerantsev, K. M. Aref'ev, D. B. Achmedov *et al.*, Fundamentals of the Practical Combustion Theory, Energoatomizdat, Leningrad, 1986 (in Russian).