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The Effect of Thermal Pretreatment Process on Bio-Fuel Conversion

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1. Introduction

In Russia exploitation of local low-grade fuels assumes the usage of bio fuels for a variety of purposes. The development of advanced combustion and gas-generating facilities operating on low-grade fuel requires the knowledge of burning and gasification processes in moderate low-temperature combustion modes.

As is known, the amount and quality of fuel particle surface open for reaction with oxidizing agent is most important for the rate of thermochemical conversion. Under comparable conditions the fuel having the largest reaction surface will have the highest rate of burn out. In qualitative terms, the properties of internal surface that formed long before it entered the furnace (reactor) and those that are forming directly in the furnace may differ. Gasification of the above fuels in autothermal mode produces gas with high content of complete combustion products (CO_2 and H_2O) and hydrocarbons and low chemical efficiency. To rise the efficiency it is necessary to implement allothermal conditions, to improve heat recirculation. To study marginal allothermal conditions ("ideal gasification") and the ways of their control a number of experiments and calculation-based estimates were made.

2. Experimental procedure

The experiments were performed on "model fuels" that differed greatly in their thermal and kinetic properties. Low-ash high-reactivity bio fuels of medium (wood) and high (dates seeds) density and products of their treatment (charcoal) were used to study the affect of pyrolysis kinetics, material density on formation of coke-ash residue reaction structure. Charcoal as oxydizing pyrolysis product entering the reaction zone of gas generators was used for investigation of gasification modes with different blow conditions. Fuels characteristics are given in Table 1.

Conditions of porous structure formation and porosity during preheating (devolatilization) were studied based on biomass particles with equivalent size $d_p \approx 10$ mm. The particles were heated by two methods: fast heating by placing the particle in muffle furnace preheated up to preset temperature (100, 200, ... 800 °C with accuracy ± 20 °C) and slow heating simultaneously with muffle heating under conditions of limited oxidizing agent supply. This allowed to simulate real conditions of thermal processes i.e. fast heating (for instance, particle pyrolysis in

fluid flow- or fluidized bed-type carbonizer) and slow heating (when the particle enters a cold fluidized bed and gets warmed gradually with the fluidized bed). After cooling the porosity was measured (mercury porosimetry: volume and sizing the pores with $d > 5.7$ nm) and specific surface area (nitrogen adsorption: surface area of pores with diameter $d > 0.3$ nm).

Parameter	Charcoal	Wood (pine)	Wood pellet	Date seed
Original particle				
Moisture of fuel as received W^{ar} , %	1.4	8	10	4
Ash (dry basis), A^d , %	0.9	1	2	0.97
Volatile content V^{daf} , %	15	88	87	85
Low heat value Q^{daf} , MJ/kg	31.5	18.1	17.5	18.9
Apparent density of fuel as received ρ , kg/m ³	380	520	1200	1150
Porosity Π , %	75	65	20	25
Specific surface area S_0 , m ² /g	8.6	1.0	2.0	0.01
Coke-ash residue after pyrolysis (fast heating/slow heating)				
Ash content A , %	NA / 1.5	NA / 3	NA / 6	NA / 2
Volatile content V^{daf} , %	NA / 1	NA / 1	NA / 1	NA / 1
Apparent density ρ , kg/m ³	280 / 320	230 / 260	NA / 360	200 / 620
Porosity, Π , %	80 / 77	85 / 83	NA / 70	87 / 60
Specific surface area S_0 , m ² /g	NA / 29.2	454 / 366	NA / 436	NA / 9.1

NA - not available.

Table 1. Model fuels characteristics

Kinetics of conversion in combustion mode was studied on individual particles with equivalent diameter $d_p = 3\text{--}75$ mm. The range of diameters examined corresponds with values showed in (Tillman D.A., 2000) as allowed for individual and co-combustion (gasification) of biofuels. Test sample placed (centered) on thermocouple junction (Ch-A type) was brought into the muffle which was preheated up to preset temperature (100, 200, ... 800 °C with accuracy ± 20 °C). The tests were performed with air flow rate 0–3.5 m³/h (upstream velocity of the flow is 0–0.5 m/s in normal conditions). Average effective burning velocity for coke-ash residue was calculated as loss of coke-ash residue estimated weight per surface unit of equivalent sphere (based on original size) during coke-ash residue burning out: $j = \Delta M / (\Delta \tau_{car} F)$. Coke-ash residue (CAR) burn-out time ($\Delta \tau_{car}$) was estimated by thermograms (fig. 1.) as time interval between points C and D. The length of A"-B segment was not accounted for.

In some aspects, individual particle burning, combustion in fluidized bed and in flame, may be assessed on the same basis. Both in flame and in fluidized bed the fuel particles are spaced at quite a distance from each other and are usually considered as individual particles. The intensity of heat-mass-exchange of particles burning in FB inert medium is comparatively close to individual particle intensity. Application of experimental data for individual particle burning to calculation and assessment of thermo chemical pretreatment of large-size particles in furnaces with dense bed is justified by the fact that heat-mass-exchange processes in its large size elements are the same as for individual particle, within the statement of the problem. Therefore the experimental data on individual particle

burning are usually used in calculations to assess thermo chemical pretreatment of large particles in furnaces of various types.

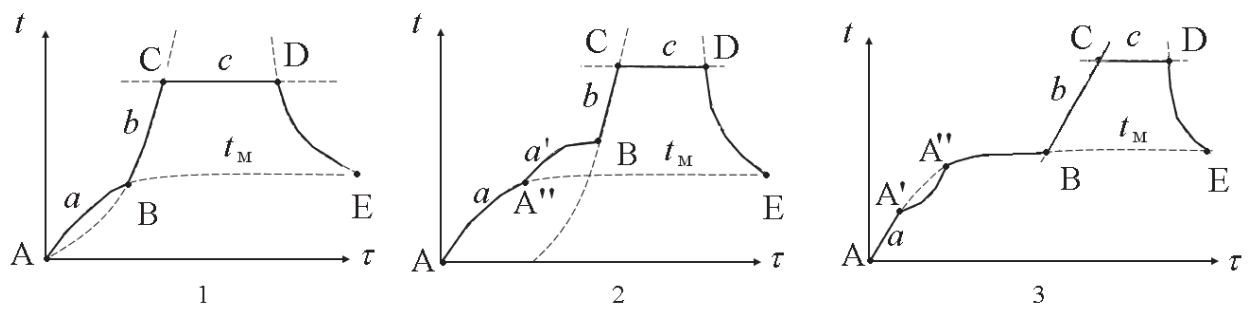


Fig. 1. Schematic view of fuels thermograms at $t_m = 400\text{ }^{\circ}\text{C}$; Moments when: A – the particle enters the furnace, A' – endothermic reaction starts to dominate, A'' – process returns back to curve of inert matter heating curve, B – intense oxidation (self ignition) of coke ash residue begins, C – quasi-stationary burning of coke-ash residue begins, D – coke-ash residue has burnt out, E – ash cooled down to muffle temperature. Processes: a – heating by inert matter curve, a' – heating due to pyrolysis gases burning; b – self-heating of coke-ash residue, c – quasi-stationary process of coke-ash residue burning; temperature in particle center t , $^{\circ}\text{C}$; time since the moment the particle entered the muffle τ , s

Experimental data was compared with other researches' data on thermal pretreatment of low-grade fuel particles in the air showed in Table 2.

No	Material (method)	Particle size, mm	Environment temperature, $^{\circ}\text{C}$	Speed of blowing, m/s	Re_d
1	Charcoal (IP)	3-80	250-1200	0-0.5	11-43
2	Wood (IP)	3-80	250-1200	0-0.5	11-43
3	Pellet (IP)	13	250-1200	0	0
4	Date seed (IP)	11	100-1200	0	0
5	Pellet (IP)	13	600-1000	0.18	10-24
6	Charcoal (IP)	3-5	280-335	0	0
7	Brown coal (FB)	2.5-5.15	800-950	0.23-0.46	2-11
8	Brown coal (IP)	0.1-1.2	850	0.01	0.004-0.05
9	Brown coal (IP)	0.1-1.0	950-1200	0.02-0.03	0.008-0.13
10	Antracite (IP)	0.1-1.0	950-1200	0.02-0.03	0.008-0.13
11	Antracite (FB)	2-9	750-950	0.54	8-40
12	Antracite (IP)	15	1000-1500	0.27-1.0	18-65
13	Fossil coal (FB)	2-10	800	0.25	4-20
14	Carbon (IP)	5.5-8.5	850-1450	0.01-10	0.5-700
15	Graphite (IP)	15	800	0.6	69
16	Electrode C (IP)	15, 25	1300	0.02	1.3-2.2

Table 2. Experimental data on thermal pretreatment of particles in the air (IP – individual particle, FB – fluidized bed)

Kinetics of conversion in gasification conditions was studied at the plant consisting of quartz retort with inner diameter 37 mm, length 650 mm, located in cylinder-shape muffle furnace ($N_{el} = 2.5$ kW, $T_{max} = 1250^{\circ}\text{C}$), air blower ($Q_{max} = 6$ m³/h, $H_{max} = 0.6$ m), electric heater, steam generator, rotameter, a set of thermocouples, carbon dioxide cylinder and thermocouple polling and temperature recording system. Combustible gas components (CO , H_2 , CH_4) were determined by gas chromatograph, air flow coefficient was determined by effluent gas composition.

The experiments were performed in dense bed which provides for the most strict fulfillment of fuel thermochemical pretreatment as stratified process, stepwise and in compliance with temperature and concentration conditions, without flow disturbances and fluid mechanics problems. Gasification was based on downdraft process. Particles with initial diameter, varying from 3 to 20 mm in different experiments, were placed in retort having a tube welded to its bottom for gas release and sampling for analysis. Fuel bed was heated in muffle furnace up to 600 – 1000°C (the temperature depended on experiment). Gasifying agent (air, air and water vapor, water vapor, or carbon dioxide) was fed via furnace tuyere inside the bed to a different depth. Blown fluid was heated by electric heater up to 700 – 750°C . The experiment was considered to be completed at the moment when CO and H_2 content in gas lowered by less than 1% of volume.

3. Experimental results and their analysis

3.1 Fuel structural transformation by pyrolysis

Pyrolysis causes significant changes of physical and chemical properties of fuel particles. Measurements showed a two-fold reduce of bio-fuel particle density in a narrow temperature range. Particle shrinks insignificantly, not more than 30% of its initial size. Since the change of volume does not exceed 20% of initial value, whereas the density decreases greatly, the porosity of particles increases. Due to pore opening the oxygen can reach new surface which was inaccessible earlier (fig. 2).

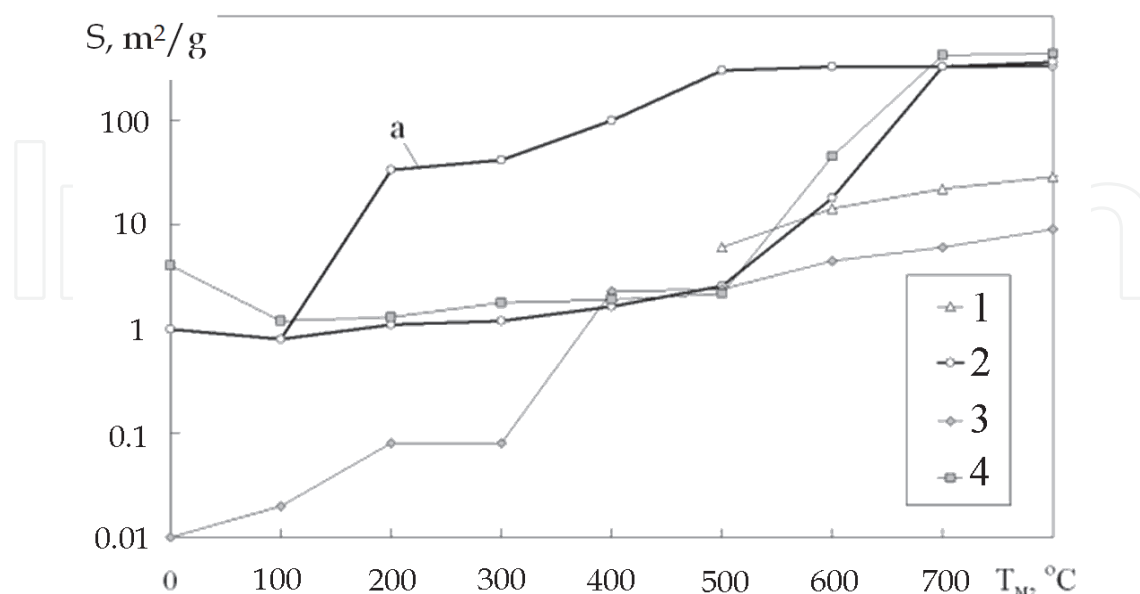


Fig. 2. Specific surface area of fuels during heating. Symbols: 1 – charcoal; 2 – wood chips, 3 – date seeds, 4 – wood pellet; a – fast heating, others – slow heating

In the range from 200 to 700°C the specific surface area of wood chip greatly depends on rate of heating, i.e. in case of fast heating it will be one or two orders higher than area during slow heating. Fuel porosity curves (fig. 3) for test samples revealed three steady peaks at 5–50, 100–3000 и 10000–50000 nm in mezzo- and macro porosity domain (5–50000 nm).

The porosity of the first nanolevel is typical of dense fuel particles. For most coals the pores' average diameter is within 4–10 nm, and more rarely in the range of 30–40 nm. Artificial materials with such pores are highly-scorched activated coals intended for absorption of large molecules such as organic dyes. When a particle enters the furnace the volume of pores of this class will greatly increase due to thermal decomposition of organic compound which is initiated by temperature rise and depressed with pressure increase being a natural regulator of gas formation process in material pores.

Nuclei of pore formation at nanolevel are thinner pores and cracks and it is within their volume that the detachment of gaseous “fragments” of splitting macro molecule of coal material occurs. Initial size of these pores is close to that of gas molecule diameter (0.4–1.0 nm). Cavity degasification process is retarded by molecular repulsion forces hindering the pass through “contracted” points in ultra microcracks and requiring great energy (activation) to overcome them which results in change of the state of dispersion phase. Materials with flexible structure (wood) form swollen-state colloidal systems resistive to both contraction and further expansion. In solid materials (cokes) structures similar to those observed in metals of interstitial compounds can be formed. The speed of gas diffusion from these pores depends on activation energy and temperature level. Gas molecule travel during typical in-furnace process time is compatible with the size of coal macro molecule.

Gas emission from numerous ultra micropores into larger ones acting as collectors continues during the entire particle burning period.

Significant flow resistance due to system porosity results in intra-pore pressure rise (up to saturation pressure) at initial destruction stage and in development of positive flow in the largest pores that hinders external gas inlet into particle pores. Simultaneously mechanical (rupture) stress may develop in the particle. With destruction process transit in its damping stage and intra-pore pressure reduction, pyrolysis gaseous products will be able to react with external oxidizing agent not only on the surface of the particle but inside the latter creating quite favorable conditions for homogeneous intra-pore burning.

As soon as degasification process is completed, free molecule diffusion (Knudsen diffusion) mode is established in nanolevel pores, coupled with convective Stefan's flow. Based on numerous estimates, for particles from 10 to 1000 μm the degree of such porous space (with specific surface area S_p) participation in reaction insignificantly depends on particle size and at 600 °C it is for oxygen within the range of $S_p / S_{\text{car}} < 0.1$ (for fast heating cokes) and $S_p / S_{\text{car}} < 0.03$ (for slow heating cokes).

Pores of the second (medium) peak ($d_p = 0.1\text{--}3 \mu\text{m}$) occur in the domain of transition from Knudsen mode to normal diffusion. They provide a better access for oxidant and can participate in reaction in larger volume. In pores of the third peak ($d_p > 10 \mu\text{m}$) diffusion runs similar to that in unrestricted space. These pores constitute insignificant part of internal surface and their contribution to burnout rate is known to be negligible. However, their role is quite significant as they can deliver reagent to joined pores of first and second peaks.

The obtained data show that wood particles and pellets have low-porous structure ($S_0 < 2 \text{ m}^2/\text{g}$), charcoal has mesoporous ($S_0 < 8.6 \text{ m}^2/\text{g}$) and seed has dense microporous structure ($S_0 < 0.01 \text{ m}^2/\text{g}$). Specific surfaces vary quite significantly in original state but this difference tends to flatten out for products of their thermal treatment. It increases to the third order for

seed (up to 9 m²/g), to the second order for wood and its products (pellet) (400 m²/g), and negligibly for charcoal (three times).

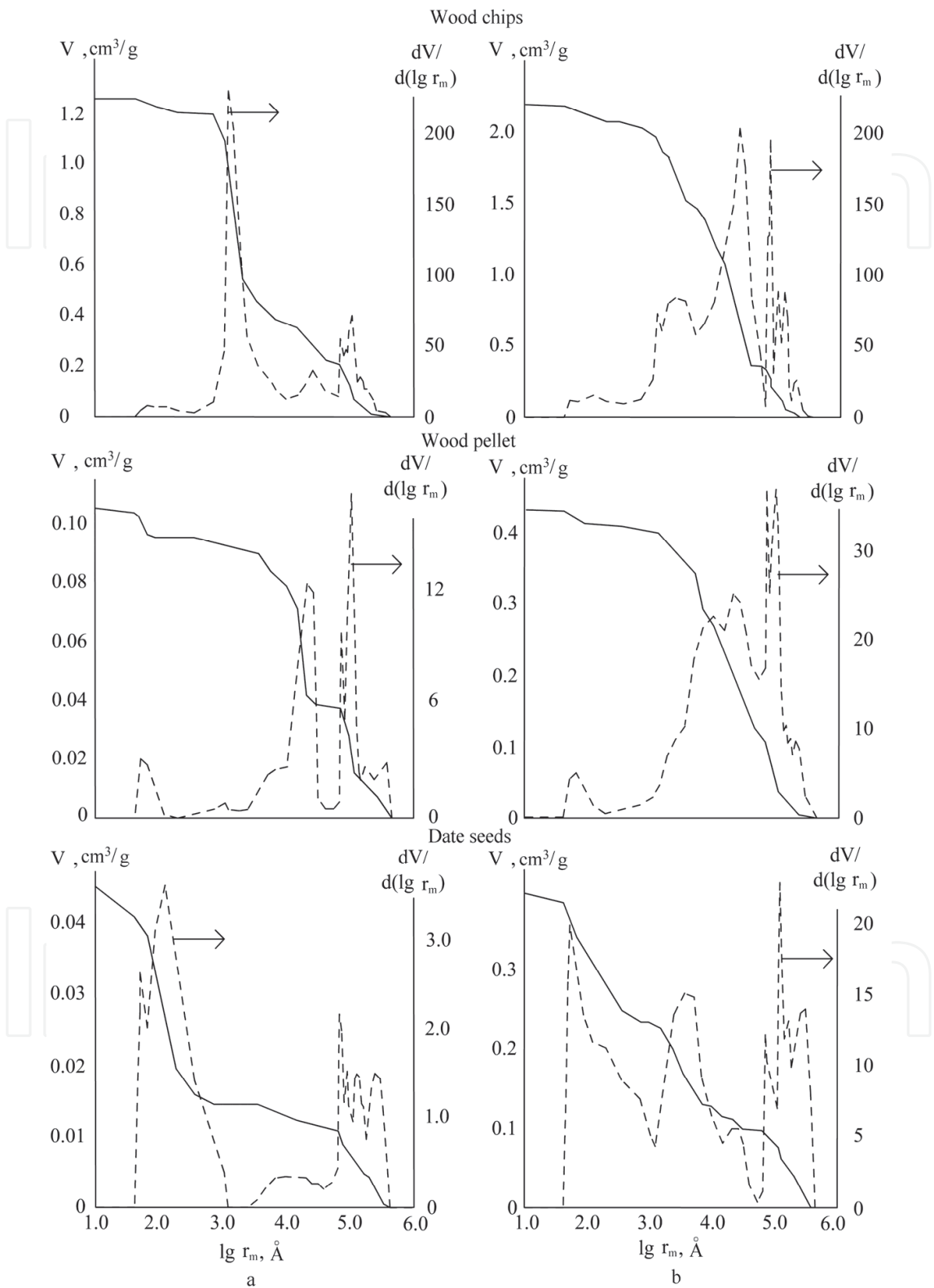


Fig. 3. Porosity curves for test fuels; pyrolysis temperature: a) 20°C, b) 800°C; r_m – medium (average) radius of pores

In seed which relates to bio fuels with the highest natural density and occupies intermediate place between wood and fossil coal the first peak pores dominate (more than 65% by volume). They are followed by the third peak pores (25%). Total volume of seed pores ($0.045 \text{ cm}^3/\text{g}$) is 2,7 times less than that of pellet ($0.12 \text{ cm}^3/\text{g}$) and 27 times less than that of the wood ($1.22 \text{ cm}^3/\text{g}$). Specific surface area of seeds is two orders lower than that of the wood. After thermal treatment the pore volume of the seed increased 10 folds and there appeared a second peak on the background of the first and the third peaks which is compatible with these two peaks, although their heights increased by one order.

In bio fuels with natural density (wood) the pores of second type dominate, whereas the pores of the first type have not been revealed and volume of the third type is insignificant. Thermal treatment of wood results in slight increase of total pore volume (twice), whereas its structure changes to form larger pores. The height of second peak reduced three times and the height of the third peak increased three times.

In pellet the structure of the wood subjected to sever mechanical processing (crushing, pressing) differs greatly from the original one, forming larger pores with drastic reduction of their original total volume (10 fold reduction). Pore distribution in pellet after thermal treatment is qualitatively identical to original one but the total volume increased 4 times and peaks became twice as high.

Comparison of porosity curves for various fuels shows that thermal treatment of bio fuels with different original structure will flatten out the difference with the formation of common transport pore structure for all fuels which may result in similar burn out rates by volume for their coke residues.

3.2 Pyrolysis thermal effects

Thermo-gravimetric analysis (TGA) was used to trace the fine dynamics of conversion (mass transfer) of small-size fuel particle ($Bi < 0.1$) at controlled temperature in thermally inert medium with hindered oxygen access (which prevent particle overheating and its premature burn-out) and mass transfer correlation having the value and sign of thermal effect.

Experiments were performed at installation Q1500D (Hungary) according to standard procedure in air medium (ground fuel sample weight was 100 mg, inert medium charge – 400 mg, temperature rise at a speed of 0.3 K/s , and final temperature 1000°C). The samples were wood particles, seeds and charcoal, products of their fast and slow thermal treatment by above described procedure and soot from ash box of pilot downdraft gas producer. Thermograms are shown in fig. 4.

Since the samples were actually dry, weight loss was mainly determined by coke-ash residue pyrolysis and oxidation effects. Overheating value and the sign of thermal effect were due to oxidizing exothermic processes in volatiles emitted by coke-ash residue (except the initial stage).

Steady heterogeneous burning of carbon of ground charcoal and coke-ash residue of bio fuels started at medium temperature above 350°C . For charcoal and wood particles this process is distinguished by appearance of specific temperature peak at 500°C . On having passed the peak, the burning of charcoal becomes uniform and finishes with some exposure at $T = 1000^\circ\text{C}$. Overheating curve for wood particles reproduces charcoal curve in shortened variant.

For seeds the pattern differs radically from above cited. In this case there is no overheating in the domain of volatile emission (which is weaker than with wood particles) which means that they behave like chemically inert substances. It is only at $T > 370^\circ\text{C}$ the

temperature of seed sample begins to exceed the ambient one. However, it exhibits its specific nature in this range too. Burnout curve for seeds has a low and extended (truncated) peak and a bit greater overheating in steady burning domain. Hence, the pyrolysis may be described as time extended process running in parallel with heterogeneous oxidation of coke-ash residue approximately up to 750°C.

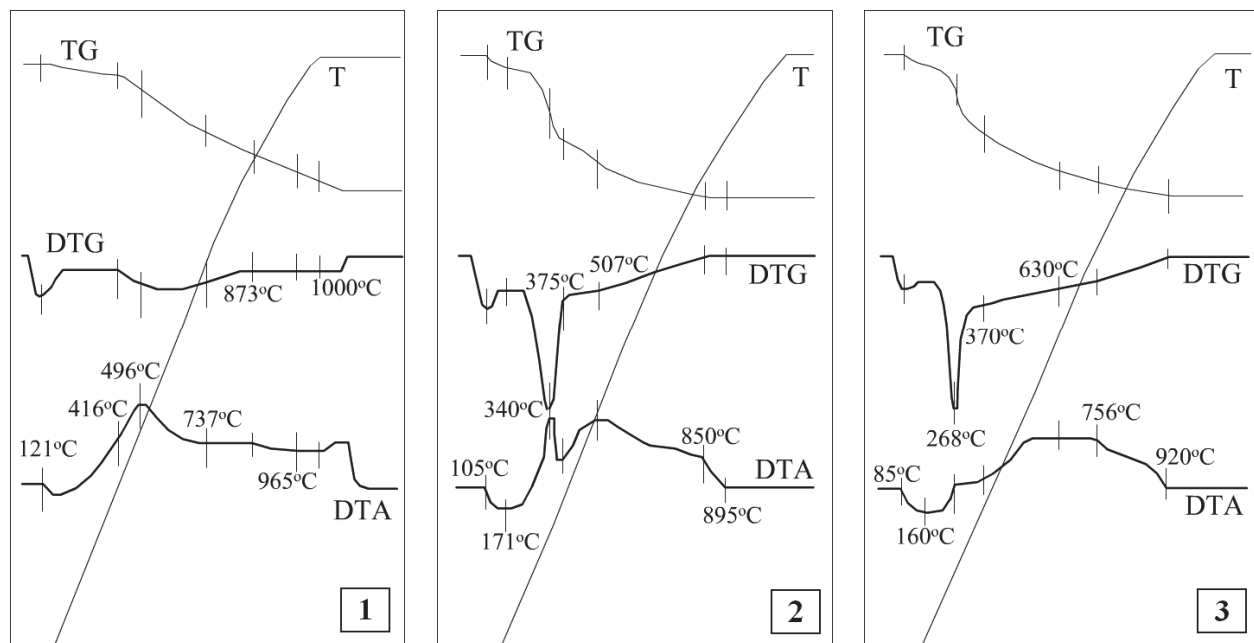


Fig. 4. Fuel thermograms: T – temperature in thermo gravimeter chamber, TG – sample weight, DTG – rate of sample weight loss, DTA – thermal effect; numbers: 1 – charcoal; 2 – wood particle, 3 – date seed

After preliminary thermal treatment according to thermal shock scenario during 15-20 minutes at 400, 600, 800°C the following was found:

Wood after thermal treatment at heating rate of 200 K/20 min retains the peak of volatile emission at 342°C, but the first (“gas”) preheating peak disappears, the height of the second peak (coke-ash residue burning) increases but the peak appears with a shift towards higher temperature domain (585°C); conversion process (weight loss) completes earlier (at 706°C instead of 850°C). Hence, the preliminary heating of fossil fuel improves its reactivity.

Charcoal after thermal treatment in thermal shock conditions during 15-20 min at 400, 600, 800°C showed that increase of thermal treatment temperature resulted in the shift of coke-ash residue peak occurrence (at 496°C instead of 462°C), heating value and conversion rate were lower, process time and final temperature were rising and the fuel partially seized to burn.

Thus, in case of thermal treatment at 400 K / 20 min the moment of coke-ash residue burn-out coincide with the moment when maximum temperature is achieved in the plant (1000°C), whereas after thermal treatment at 800 K / 15 min the burning process finishes with incomplete burn out (unburned carbon of 9%) and much later after the furnace has been warmed up to maximum.

Charcoal after thermal treatment according to “heating simultaneously with furnace” scenario is characterized by still lower burn out rate and greater unburned carbon (14%) at the same final temperature values. The behavior of solid-phase volatile decomposition

products settling in gas generator ash box (soot) is alike. Inert component content in these products (due to specific sampling conditions) reaches 50%, therefore the burn-out process finishes earlier which corresponds to 800°C.

3.3 Biofuel particle ignition

In low-temperature range (temperature in muffle $t_m = 250\text{--}500^\circ\text{C}$) from the moment the particle enters the furnace and up to pyrolysis commencement the particles are heated due to muffle irradiation as inert compound (curve *a* in fig. 1). Further in the case of charcoal the coke-ash residue will ignite (point B), with temperature upsurge (self-heating) exponentially (curve *b*) and burning in quasi-stationary conditions (curve *c*). Charcoal has the lowest volatile content and preliminary prepared (mostly) reaction surface (75% porosity and specific surface area of 8.6 m²/g). In the course of pyrolysis charcoal characteristics change insignificantly (porosity increases up to 77–80%, specific surface up to 29.2 m²/g), self-heating starts at $t_m \approx 250^\circ\text{C}$. Quasi-stationary combustion starts earlier than in the case of wood and seeds. Charcoal self-heating starts about 50 s and 400 s earlier than that of wood and seed respectively (time difference between B points).

In the case of wood having porosity close to coal porosity (65%) and specific surface one order lower (1 m²/g), heating of the particle after the temperature of intense pyrolysis commencement has been reached (particle temperature $t_p \approx 275^\circ\text{C}$) follows the curve *a'* (up to $t_p \approx 420^\circ\text{C} > t_m$). The analysis shows that at muffle temperature of 400°C the volatile combustion heat which amounts up to 60% of total heat flux plays a key role. Contribution of bio fuel volatiles combustion to warm-up of their solid residue is of major importance. At muffle temperature of 800°C the main heat flux is muffle irradiation which amounts to approximately 60%.

Intense emission and burning of volatiles hinders the access of oxygen to coke-ash residue, which has been repeatedly described elsewhere, and residue warming is less intense than in the case of charcoal. After the major portion of volatiles has burnt out (point B) the coke-ash residue of wood particle gets heated following the curve *b* with its intensity close to that of charcoal self-heating but to a higher temperature, and finally it burns out 1.5–2.0 times quicker. It should be noted that porosity and specific surface of wood coke-ash residue exceed that of the coal.

In the case of wood the sources of warming are heat fluxes from muffle furnace, exothermic reactions of pyrolysis and combustion of volatiles. The amount and ratio of these fluxes depend on muffle and particle temperature.

The time of preheating stage and solid residue combustion at 400°C are compatible for wood (~ 1 : 1). With muffle temperature increase this ratio will change towards increase of relative duration of solid residue burn out and at 800°C it will be 1 : 4. Heat emission intensity (W/m²) for volatile combustion and coke oxidation is actually 1 : 1. With temperature increase the intensity of heat emission for volatile combustion will increase significantly compared to coke oxidation, i.e. ~ 4 : 1.

Initial characteristics of seed inner surface are much lower than those of other bio fuels (25% porosity, 0.01 m²/g specific surface). Due to different thermal capacity and under endothermic effects revealed in analysis of the seed, the latter is heated more slowly on segment A'–A'' than “model” inert compound. To the right from A'' point volatiles release intensively in the form of boiling liquid tar fractions (“cuts”) in coke-ash residue pores and on the surface (as is the case with coking coals). During decomposition they partially form

soot on porous coke-ash residue surface and partially emit non-ignited as a dense smoke (of fallow color). On segment $A''-B$ within approximately 250–300 sec temperature in seed center actually coincides with muffle temperature. Formally this period is a variety of well-known induction period (Pomerantsev, 1973).

Partial overlap of reaction surface by tar fractions and much less initial porosity (see Table 1) result in notable delay of seed self-warming commencement compared to wood and charcoal self-heating. By moment B which is characterized by disappearance of liquid phase on the surface, the particle becomes accessible to air and ignition and self heating of coke ash residue commence. In this case the speed of temperature increase is almost 10 times lower than that of wood and charcoal which is apparently due to incomplete pyrolysis at previous stage. By the end of self-heating seed coke-ash residue has the greatest porosity and hence the highest overheating temperature and finally the maximum rate of burning.

For seed the duration of thermal pretreatment and solid residue burning at 400 °C is expressed as 3 : 1 (in this case the preparing stage lasts much longer than that of wood). When muffle temperature reaches 800 °C this ratio changes towards increase of relative solid residue burn out period, similarly to the ratio for wood, and becomes 1 : 4. The relation between heat radiation intensity at stages of volatile combustion and seed coke oxidation is 0.3 : 1 (volatile: coke) at 400 °C and 4:1 at 800 °C.

In high temperature range (at muffle temperature above 500 °C) the distinctions between warming and ignition of different bio fuels are smoothed. Seed warming delay relative to charcoal particle decreases actually to zero and overheating by the end of self-heating and burning rate of coke-ash residue in the main segment come closer. Qualitatively varying pyrolysis scenarios for different bio fuels with close quantitative result for burning intensity are of less importance which correlates well with a well-known high-temperature experiment. The processes of wood particle and seed ignition are qualitatively different to a large extent and they both differ from charcoal ignition. Visual examination shows that after wood particle is placed in muffle at 800 °C volatiles release is slow with formation of “faint” burning layer close to surface and slightly fluctuating short flame above it (compatible with particle diameter). Volatile release from seeds has “explosive” intensity with continuous burning substance burst out to the distance of up to 3–4 diameters of seed (Fig. 5)

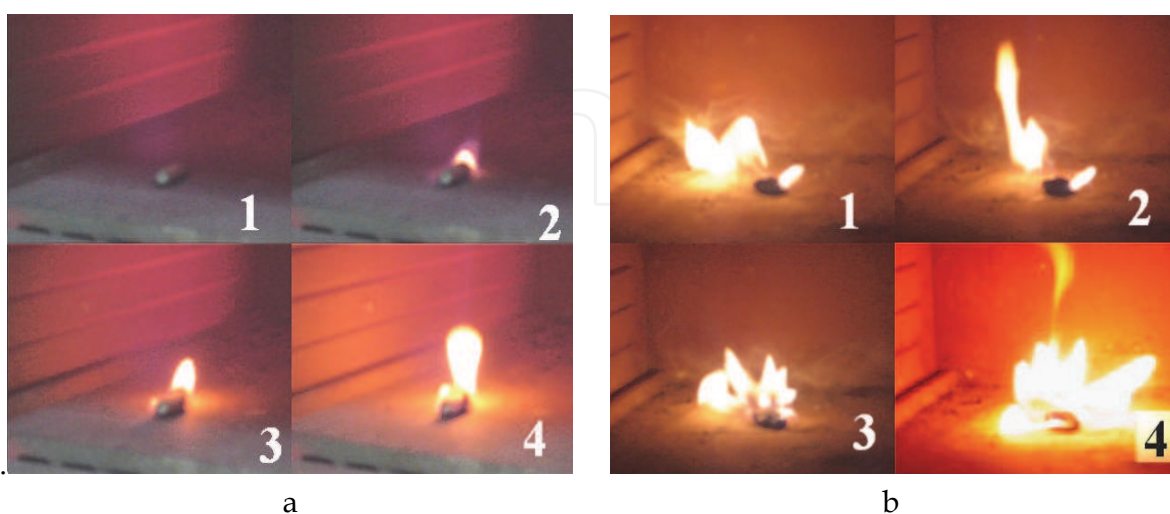


Fig. 5. Process of inflammation: a) wood chip, b) date seed; 1-4 – stages of inflammation from time of placing particle into the muffle (1) separated by 20 s.

3.4 Kinetics of coke-ash residue conversion in burn out conditions

Visual observations of a single particle show that irrespective of low ash content wood chips burn out inside ash enclosure under natural convection conditions: the size of burning carbon nuclear gradually decreases and remaining ash (soft) enclosure retains the original shape of the particle, actually without changing the size. This effect is reached in intense turbulent fluidizing bed too, but when high-ash flotation tailings with rigid mineral enclosure are burnt (Belyaev A.A., 2009).

In low-temperature range the burning of wood and seed coke-ash residues begins after the major portion of volatiles releases at particle temperature $t_p \approx 350\text{--}400$ °C; for charcoal with small volatile content the burning starts at lower temperature $t_p \approx 250\text{--}300$ °C. Coke-ash residue burning at temperature close to above cited values in intra-kinetic mode exhibits significant overheating of particle center relative to environment temperature: $\Delta T = 360$ °C for seed, 250 °C for wood, 300 °C for charcoal (6,a).

In high temperature range with dominating diffusive resistance the overheating of particle center relative to environment is negligible: at 800 °C it is equal to $\Delta T = 145$ °C for pellet and seed, 105 °C for wood, 85 °C for charcoal, at 1200 °C it is 75 °C for wood, 40 °C for charcoal. Transfer from kinetic to intra-diffusion conditions is most pronounced for charcoal, as its combustion is not aggravated by volatile release in great amounts and actually represents coke residue burn out. Burning rate curve has a “knee” in the range of environment temperature of 400 °C ($t_p = 600$ °C): steep segment corresponds to kinetic mode and flat segment to diffusion mode (fig. 6,a).

In high temperature range the maximum overheating of particle center at $t_m = 800$ °C is found for seed having maximum porosity after pyrolysis and minimum overheating is exhibited by charcoal which appears to have the least porosity and lowest reactivity by the moment when stationary burning conditions are achieved, compared to any other examined fuel. Overheating of wood particle center is between these two values. Burn out rate ratio for examined fuels are in correlation with the ratio of porosity of examined fuels coke-ash residue porosity relation in point B of thermal curves, similar to overheating relations (table 1, porosity after fast heating).

Fig. (6,b) shows the rate of burning and overheating (fragment) *vs* blow rate in high temperature range. Air speed variations in the range from 0 to 0.5 m/s result in approximately two-fold change of burning rate and overheating of examined fuels. Irrespective of extremely low ash content, the wood particle at zero blow speed burns out inside ash envelope: carbon-including portion shrinks and ash enclosure builds up actually retaining the shape and the size of original particle.

At blow speed equal to 0.1 m/s and more the ash envelope is thrown away by air flow opening the coke-ash residue which is similar to ash enclosure behavior in case of anthracite, charcoal and electrode coal particles combustion. Charcoal burn out rate is lower than that of bio fuels coke-ash residue in the entire range of examined blow speeds.

The mode of fuel thermo chemical conversion which is similar to examined mode without blow is typical of fluidized bed gasifiers and complete combustion furnaces after the blowing has stopped by some reason and low-intense residue burn-out continues for many hours (with fire bed surface intensity $q_R < 0.3$ MW/m²). Examined modes with blow speed about 0.5 m/s in normal conditions are marginal case of blowing for ordinary FB furnace without bed stability loss and maintain fire bed surface intensity $q_R \approx 4$ MW/m². Experimental results were used by the authors for designing the up-to-date gas generator firing the wood fuel. Fig. (6,c) shows the burning rates *vs.* particle temperature.

Experimental points are located within the "segment" limited by lines of kinetic and diffusion modes. Wood burning rate in high-temperature conditions at $t_p = 900$ oC and $w = 0$ m/s is less than estimated speed limit in diffusion mode by approximately 5-15%, charcoal rate by 10-30%.

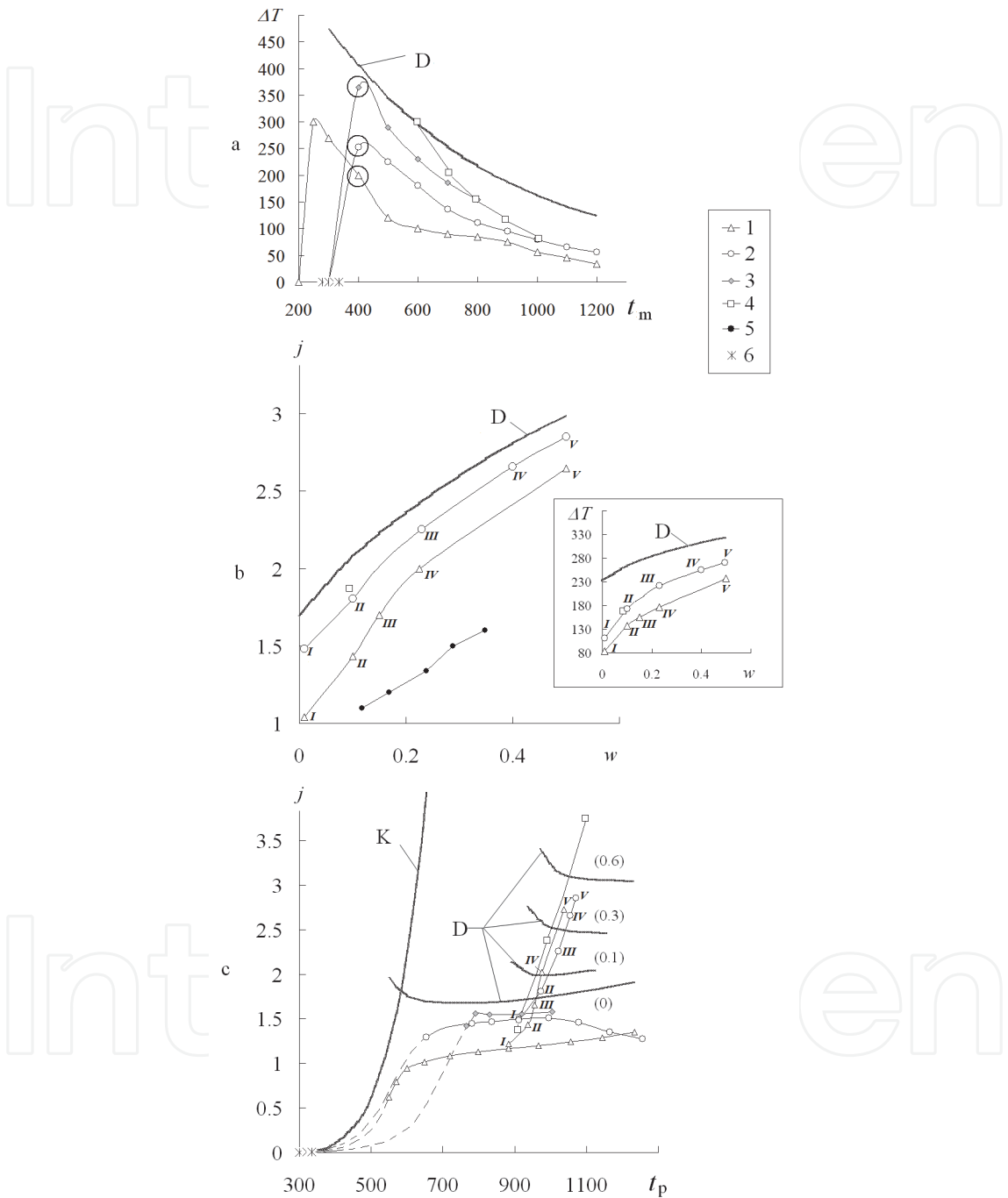


Fig. 6. Curves: a) particle center overheating, °C vs muffle temperature, °C, with blow speed $w = 0$, m/s, b) coke-ash residue burning rate j , g/(m²s) vs. blow speed w , m/s, at $t_m = 800$ – 900 oC, c) coke-ash residue burning rate j , g/(m²s) vs. particle temperature t_p , °C (numbers in brackets indicate blow speed, m/s); designations are per table 2; the fragment shows particle center overheating ΔT , °C vs. blow speed; roman numbers are numbers of experiments; D – diffusive mode, K – kinetic mode

Fig. 7. shows the particle burning rate j , g/(m²s) vs. reverse ($1000 / T_p$, 1000 / K) and normal (t_p , °C) temperatures of particle.

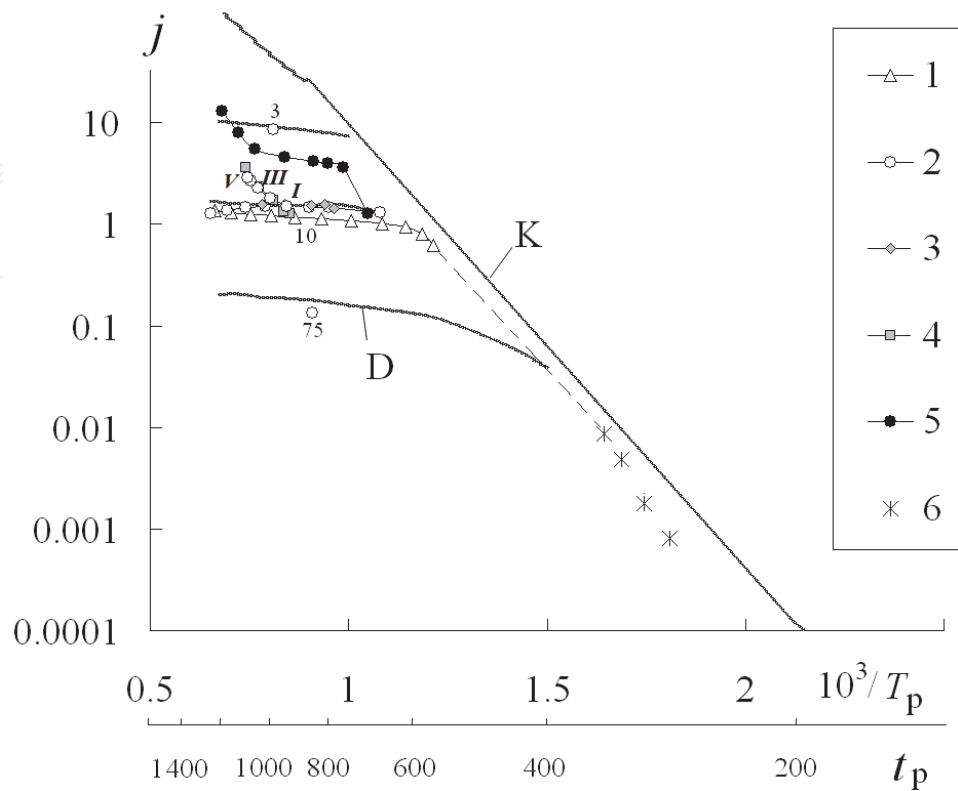


Fig. 7. Particle burning rate j , g/(m²s) vs. reverse ($1000 / T_p$, 1000 / K) and normal (t_p , °C) temperatures of particle; numbers in brackets designate particle diameter, d_p , mm; symbols are per table 2; roman numbers designate burning with blow, the same as in fig. 6

Our data on charcoal at $t_m = 300$ – 1200 °C are grouped close to calculated curve for diffusion mode, and charcoal points received at $t_m = 280$ – 335 °C (Khitrin, 1955) at lower oxygen content in heating medium with burn out without flame-forming self-heating are closer to kinetic curve. Superimposing of experimental points for coal on one curve show that particle temperature shall be chosen as key value in calculations. Choosing the key temperature is important for processing the experimental data in Arrhenius coordinates, because this determines the slope of curve. Choosing the particle temperature as key temperature is important for the range of medium temperatures from 300 to 700 °C where significant overheating occurs. Brown coal particles with diameter $d_p = 3$ mm in FB within temperature range of $t_m = 400$ – 900 °C burns out in intra diffusion mode. Due to lower reactivity of brown coal coke-ash residue the rate of its burning in intra diffusion mode is almost half of wood coke-ash residue burning rate with $d_p = 3$ mm, and transfer to intra kinetic mode occurs at temperature that is higher by 150–200 °C.

Diffusion behavior of bio fuel combustion at environment temperature above 500 °C is observed in the entire examined range of particle diameters, $d_p = 3$ –75 mm. Review of the results obtained in different studies demonstrates that in temperature range from 800 to 950 °C fine particles (with sub millimeter diameter) exhibit kinetic mode of burning. Thus, according to fig. 8, the actual overheating of coal dust is below calculated values (line 1). Calculation with actual burning rates (line 2) is close to actual overheating values.

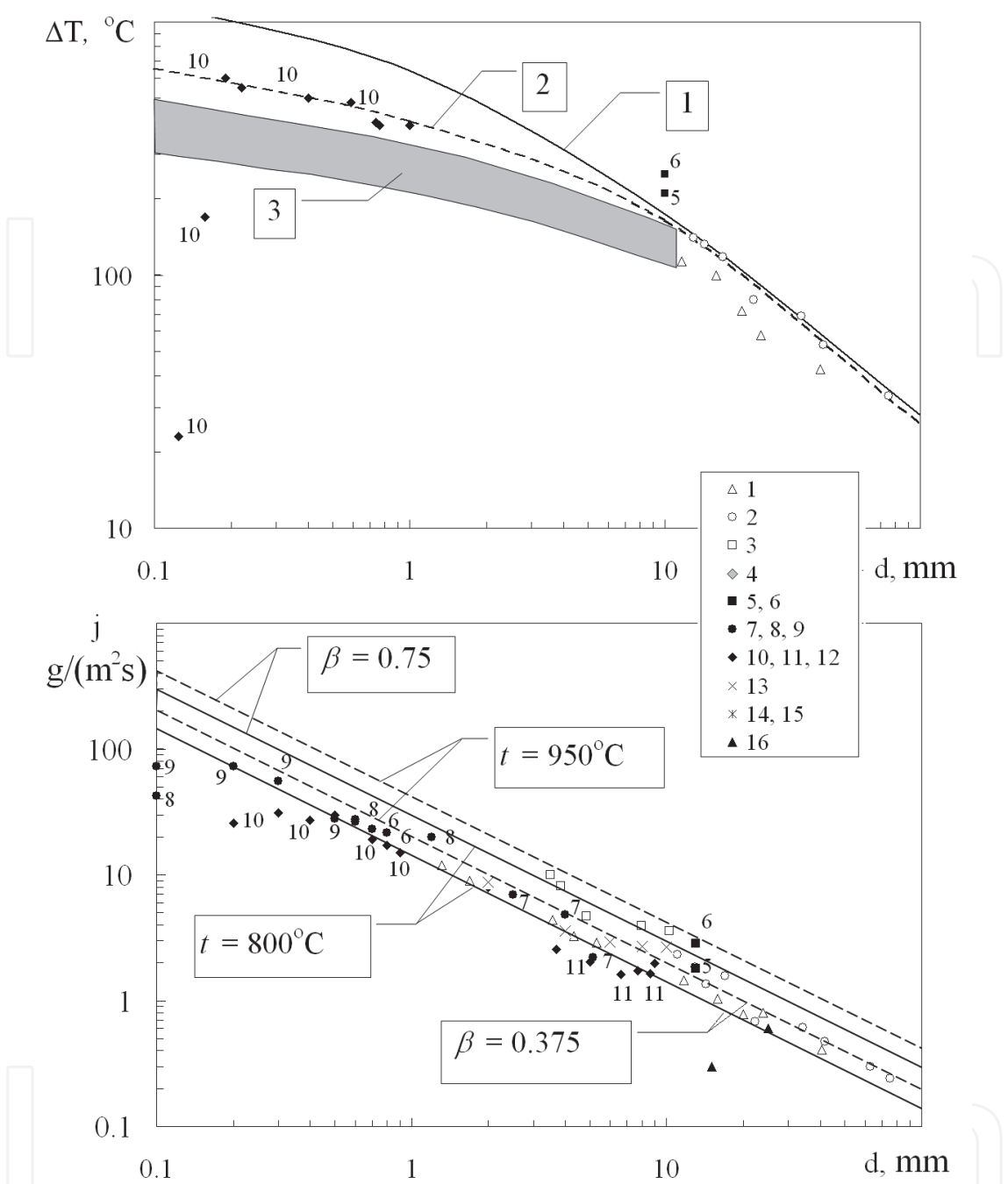


Fig. 8. Overheating and burning rate vs. particle size: 1 – calculated, 2 – ditto for actual burning rates, 3 – calculation for FB with inert material diameter from 0.4 to 1.5 mm. Numbers are per Table 2

With particle size increase its specific surface decreases (per volume unit) and boundary layer becomes larger. This causes decrease of specific heat emission, overheating and burning rate and the particle approaches to isothermal burning. With diameter changing from 10 to 75 mm at $T_m = 800^{\circ}\text{C}$ the overheating lowers from 120–150 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$, and burning rate from ≈ 2 to ≈ 0.2 g/(m²s). In the range of $d_p = 10\text{--}75$ mm calculation with accuracy of $\pm 15\%$ is approximated by dependence $\Delta T = 1130 \cdot d_p^{-0.84}$, $^{\circ}\text{C}$ and $j = 23 \cdot d_p^{-1}$, g/(m²s). Diameter d_p is expressed in mm.

The available results for FB were obtained with fluidization rate which is much higher than the rate of natural convection. The structure of flows in FB is quite specific (Sherwood criterion for inert medium at rest tends to 1.0). At $Re = 80$ and higher the burning of particle in FB and in inert-free medium occurs with close dimensionless rates, at small Reynolds numbers the burning in FB is less intense than in inert-free medium and occurs with overheating approximately half as much. This is why the estimated set of overheating (field 3 in fig. 8) depending on inert substance particle diameter (from 0.4 to 1.5 mm) is in satisfactory agreement with general dependence for individual fuel particle within a wide range of its diameters but is well below than actual data for dust burning by V.I.Babiy (Babiy, 1986). Overheating of pellet in FB (point 5) is greater than that of wood particle of approximately the same size in natural convection which may be associated with higher density of the pellet (Palchonok, 2002).

Fig. 9 demonstrates generalized relations “dimensionless burning rate vs Reynolds number” at medium temperature 400–1500 °C, with particle diameter $d_p = 0.1\text{--}80\text{ mm}$, blow rate $w = 0.01\text{--}50\text{ m/s}$. Data by V.I. Babiy for dusts can be generalized by his curve if medium temperature is assumed to be key temperature. Calculations based on particle temperature as key temperature (domain 5 in fig. 9) makes his points lie below his own curve. This means that burn out of dusts at these temperatures occurs in kinetic mode. Experimental data by L.I. Khitrin lie close to his curve.

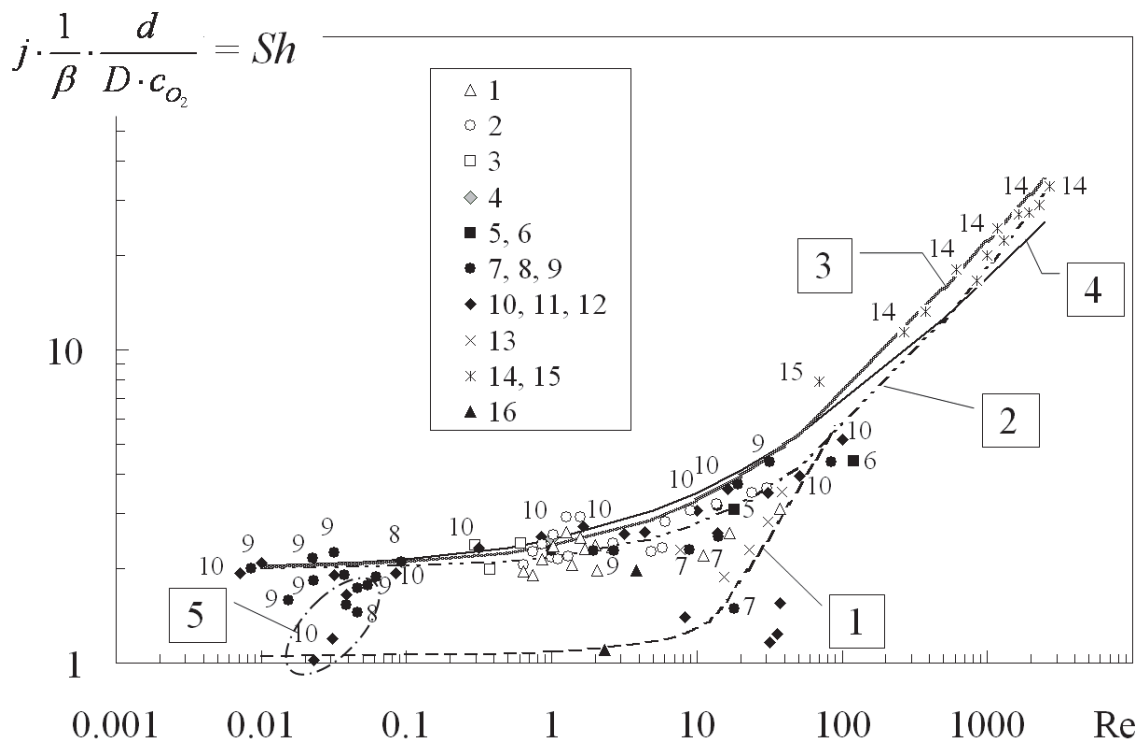


Fig. 9. Dimensionless rate of burning vs. Re number: 1 – calculation for FB, 2, 3, 4 – calculation data; 5 – V.I. Babiy points at particle key temperature; numbers are per Table 2

3.5 Kinetics of coke-ash residue conversion in gasification mode

Gasification process was realized with intermittent charging, gas composition changed with bed burn out: first, combustible content raised, but on having reached (at some definite bed depth) maximum value, it began to decrease (fig. 10,d).

Coal bed depth in retort at which H₂ and CO contents began to decrease was equal to 6 to 7 initial size (average equivalent diameters) of fuel which corresponds to available reference data. At bed depth equal to 1–3 particle size CO content lowered down to 9–10%, and H₂ content approached zero with the accuracy within instrument error range. The depth of 1 to 3 sizes was in compliance with available data on burning zone height.

For two blow types (air and steam-air) charcoal conversion gas composition dependence on air flow rate in maximum concentration point (for bed depth of 6–7 sizes) was studied (fig. 10,a,b). A series of experiments was conducted with sequential blow increase in every next experiment. The greater air flow rate and hence the higher temperature in bed corresponded to higher CO content in gas.

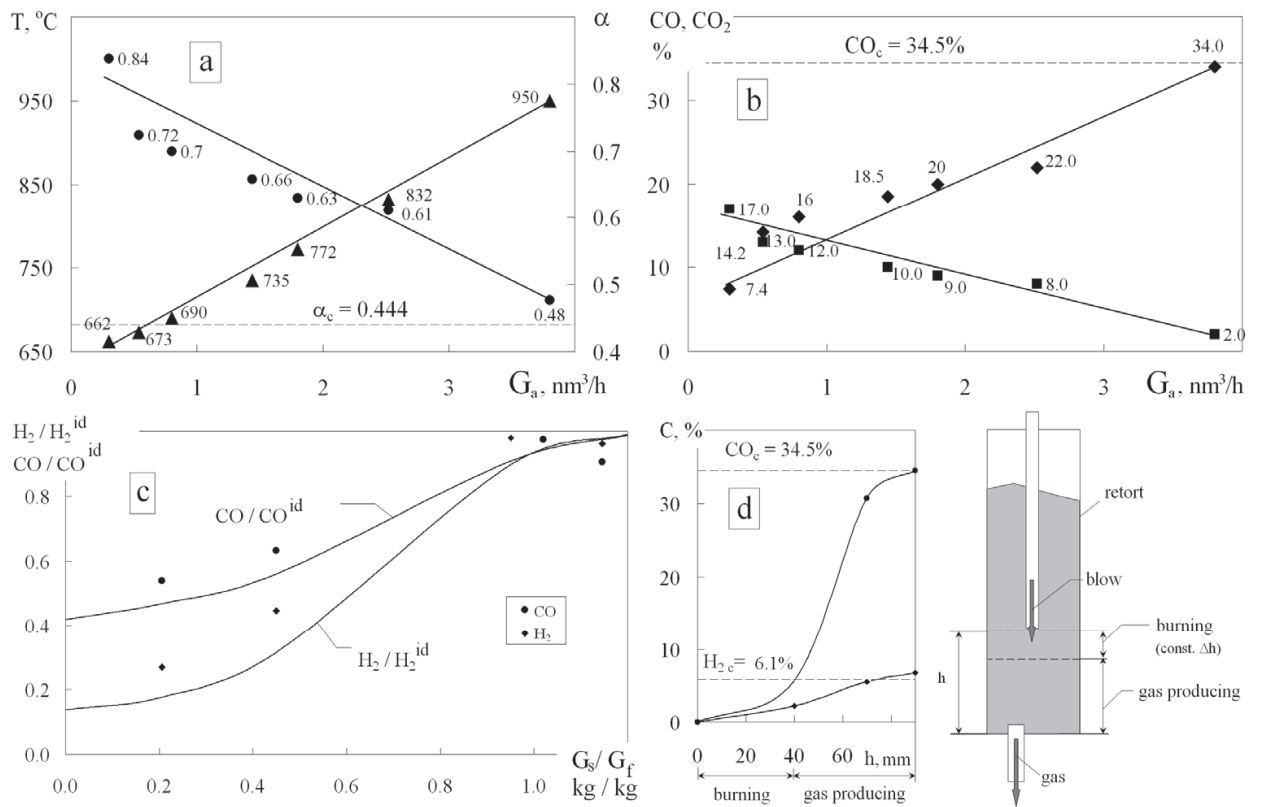


Fig. 10. Relationship between gasification parameters; air flow rate effect on: a) temperature in reduction zone (T) and air flow rate coefficient (α); b) CO and CO₂ content in gas; CO_c and α_c – maximum CO content in gas and blow-limiting factor for air gasification of pure carbon; c) H₂ and CO relative concentration in producer gas depending on steam content in blow: s – steam, f – fuel, id – ideal regime; lines represent calculation of gas equilibrium composition; d) gas composition vs. bed depth in retort

At temperature below 700°C gasification reactions actually did not occur and gas composition corresponded to pyrolysis. CO content tended to estimated limit for pure carbon with air blow ($\text{CO}_c = 34.5\%$), and blow coefficient defined by effluent gas composition was approaching α_c . Maximum concentration limits and minimum blow rate coefficient were reached at blow rate $\approx 4 \text{ m}^3/\text{h}$ (speed of blow in bed calculated for empty cross-section is 1.4 m/s) and bed temperature of 950°C.

The results explain the phenomenon of the so called rapid burning. It is believed that the higher is the blow rate in combustion process, the lower is solid-carbon based reduction of CO_2 to CO beyond combustion zone because the time needed for reduction is insufficient. On reaching a certain rate the reduction process stops and CO and CO_2 ratio in gas becomes determined by their ratio that was established in burning zone (primary CO and CO_2). Experiments with activated charcoal showed that at blow rate above 0.3 m/s CO content is 34.5%, and CO_2 is 2%. Study results allow to give a simpler explanation of “rapid gasification” phenomenon, i.e. gasification conditions can be achieved at $\alpha = \alpha_c$. The result confirms the possibility of producing gas that does not contain three-atom gases (CO_2 and H_2O) and methane, and shows one of the ways of its production in dense bed, by providing optimum depth and temperature not less than 900-950°C.

Fig. 10,c demonstrates the results of experiments on allothermal steam-air gasification in dimensionless form: gas concentration is reduced to that in gas of ideal air-steam conversion of char coal ($\text{CO}^{\text{id}} = 43\%$, $\text{H}_2^{\text{id}} = 26\%$). Steam content (G_s / G_f , kg steam/kg fuel) was increased in every next experiment with constant air supply corresponding to $\alpha = 0.7$ for dry blow (“semi-gas” mode). In this case gas was enriched with combustible components by reaction $\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$. Steam breakthrough was not observed.

At steam supply in the amount of 1-1.2 kg of steam/kg of fuel (moisture in terms of fuel as received $W \approx 60\%$) CO and H_2 content in the experiment was close to ideal steam-air concentration of 35-42% and 22-25% respectively, with chemical efficiency for steam-air conversion $\eta_{\text{chem}}=1.0$.

Fig. 11 demonstrates gas composition change with bed depth for allothermal steam (water) conversion and fig. 12 shows carbon-dioxide conversion of char coal in bed with temperature 950-1000°C and blow at temperature 600-750°C.

Gas composition for steam conversion at temperature $T \approx 1100^\circ\text{C}$ corresponds by 97.5% to stoichiometric one ($\text{CO} = 42.6\%$, $\text{H}_2 = 54.8\%$), and chemical efficiency of steam conversion $\eta_{\text{chem}} = 1.26$. Ratio of CO content to stoichiometric value for carbon dioxide conversion reached 0.8 and chemical efficiency of carbon dioxide conversion $\eta_{\text{chem}}=1.35$.

At bed depth less than 70 sizes a linear variation of CO content with bed height was detected for both carbon dioxide or steam blow. Hydrogen content does not depend on bed height and it was increasing during the entire experiment.

Allothermal technique of the experiment allowed to decompose all water steam fed into the bed due to muffle heat. In the experiments allothermal gasification marginal conditions were achieved for steam-water, steam and carbon dioxide blow. In two latter cases homogeneous gas-water shift reaction $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ was performed providing for increase of H_2 content above stoichiometric value by heterogeneous reaction and steam conversion of charcoal.

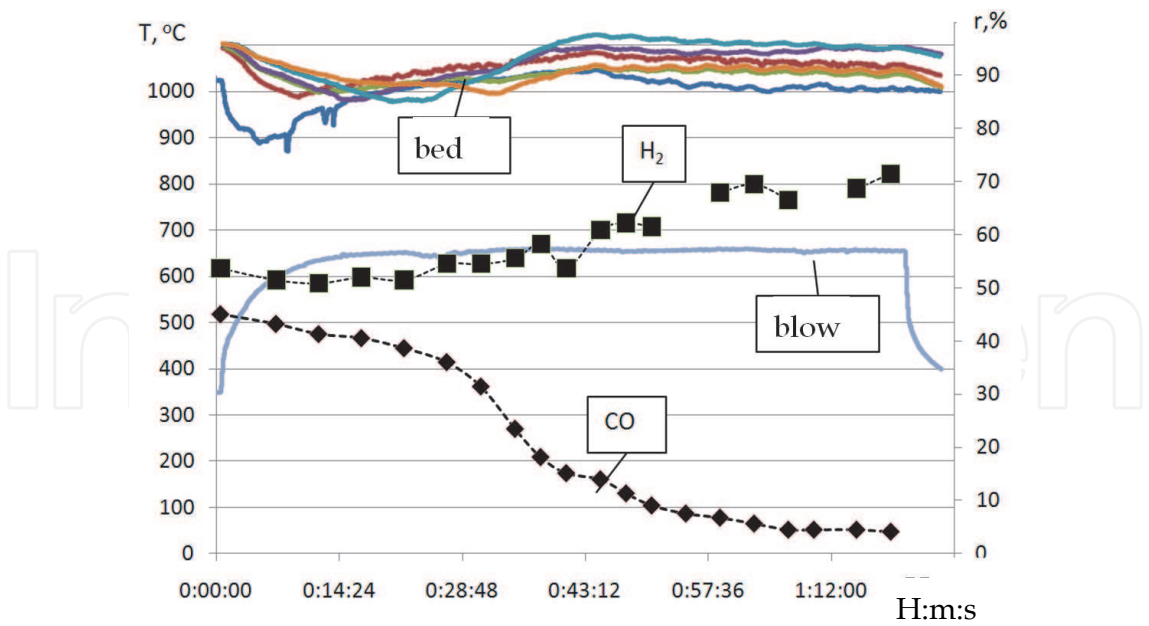


Fig. 11. Steam allothermal conversion

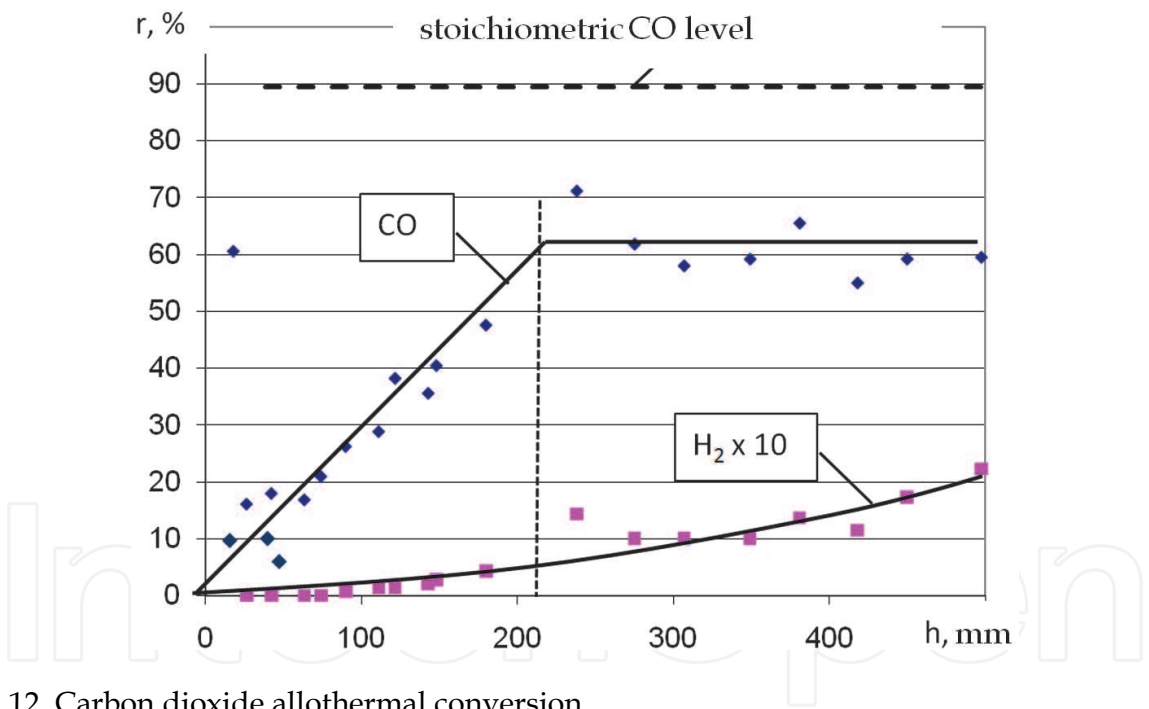


Fig. 12. Carbon dioxide allothermal conversion

3.6 Using heat recovery (recirculation) for advanced CCGT with thermo chemical conversion of low-grade fuels

Temperature limits and ranges of mass concentration of combustible elements and oxidizing agent were determined, in which the process of low-grade fuel gasification is realized with higher conversion efficiency and which include multi-parametric optimum conditions for hypothetical “ideal” tars free conversion into useful products. Fuels are divided into two groups: “A” group includes fuels that are converted into ideal mixture ($\text{CO}+\text{H}_2$) due to their own internal chemical source of heat (in auto-thermal modes) and “B” group that requires

heat power source (allo- and auto-thermal mode) for ideal conversion, moreover in case of auto thermal process the gas is not ideal and has complete combustion products (CO_2 and H_2O). Wood, peat, and some high-moisture brown coals belong to “B” group. In “A” range the ideal gasification is characterized by constant heating value of gas and constant chemical efficiency of fuel conversion into syngas, moreover, high-metamorphized fuels require considerable amount of water vapor to be added whereas the main source of molecular hydrogen for brown coals is fuel hydrogen.

Allothermal conversion procedure allows to obtain maximum effect of chemical efficiency increase (fig. 13, points 8'', 8''' and 8'''' are results of allothermal steam-air, steam and carbon dioxide gasification). However, conversion efficiency rise due to external sources is rarely used (p.p. 4', 7'), which is explained by their “high investments” and low production effectiveness.

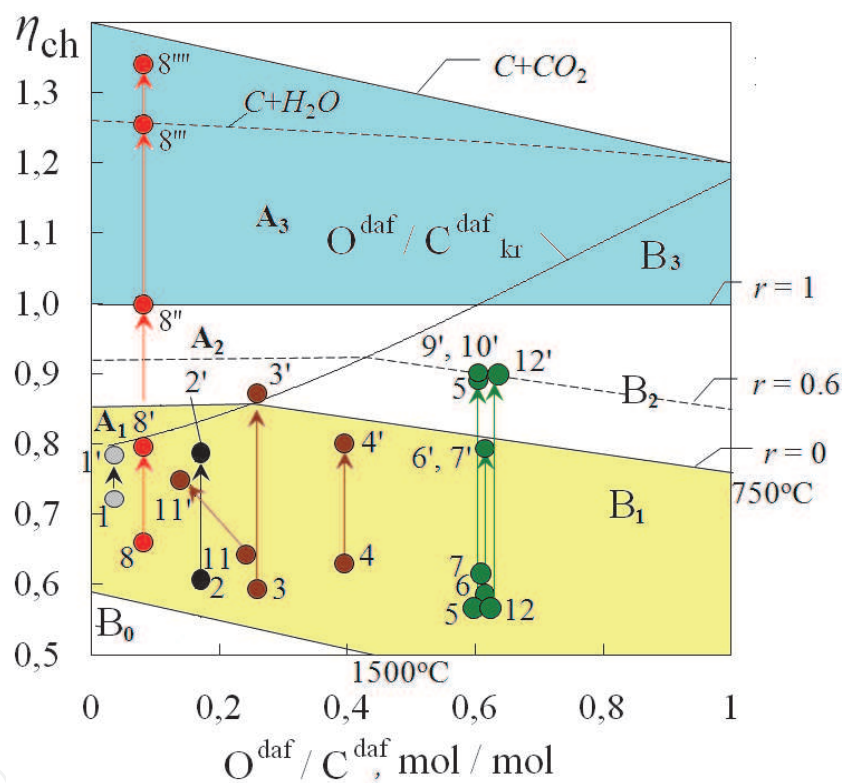


Fig. 13. Chemical efficiency of air thermochemical conversion:

1 – fuel oil gasification without regeneration in flow-type gasifier (by VNII NP); 1' – ditto, calculation with regeneration; 2 – first-generation dense-bed gasifier operating on black coal; 2' – tuyere gas producer (JSC VTI) operating on black coal; 3 – gas producer by MHI without regeneration (estimated); 3' – gas generator MHI (expected upgrading of recirculation system); 4 – first-generation dense bed gas producer operating on peat; 4' – allothermal pyrolyzer for peat OIVTAN; 5, 6, 7, 8 – first-generation dense bed gas generator; 5' – first-generation gas producer with superadiabatic heating by IPKhF RAN (estimated); 6' – upgraded downdraft producer by UrFU with regeneration; 7' – plasma gas generator, IEE RAN; 8' – three-zone downdraft producer by UrFU, 8'' – with steam and air blow, 8''' – with steam blow at 1000oC to the third zone, 8'''' – with carbon dioxide blow at 1000oC to the third zone; 9' – mini-CHP gasifier Viking, Denmark (estimated); 10' – mini-CHP gasifier, UrFU (estimated); 11 – brown coal gasification (estimation); 11' – joint gasification of brown coal and natural gas, VNII NP; 12, 12' – downdraft producer by ISEM with different blow temperatures

There is a substantial potential to rise chemical efficiency by improving heat recirculation within gas generator or "gas generator-gas consumer" system. This becomes evident when analyzing the tendencies of development of both industrial large-capacity coal gasifiers (from *Winkler* gasifier to *HTW* plant), and air gasification plants especially those working on low-grade fuels and bio mass. In simple-design (without recirculation) gasifiers operating on biomass with steam and air blow the percent of fuel needed to provide for complete combustion is great (up to 30 %), and temperature is low, therefore gas contains a considerable amount of intermediate gasification products (tars, CO_2 and H_2O) and chemical efficiency is not more than 60 %. Such reactors cannot generate gas with close to ideal characteristics even hypothetically. This is why the development of simple-procedure low-efficiency air reactors does not seem to have any perspective.

4. Conclusion

The kinetics of thermo chemical conversion was studied on low-grade fuels in oxidizing pyrolysis, afterburning and gasification modes in temperature ranges typical of moderate combustion conditions in power reactors. The obtained data were used as the basis for upgrading of effective conversion procedure which will allow to develop gasifying plants with high chemical efficiency in the long term.

The procedure for non renewable resources conversion in fuel gas for gas engines (gas turbine engines, internal combustion engines) and fuel cells has been developed. This procedure provides low tar and hydrocarbon content in gas with high chemical efficiency (80% achieved and 90-95% design efficiency) which is novel in Russia and in prospect it will allow to rise the electrical efficiency of small scale CHP up to 23-25% on bio fuel and up to 50% on fuel cells, and the efficiency of large scale brown-coal CCGT and IGCC up to 50-55% and will make them competitive.

The procedure was implemented at multi-zone dense-bed gasifier with capacity up to 200 kW for bio mass and peat fuels and in a group of pyrolysisers having capacity of 10 MW each for pulverized carbon-rich black coal with after-burning of conversion products in coal-fired boiler with capacity of 420 tons of steam per hour.

Small-scale gasification studies are aimed at designing of CHP-ICE with electrical output up to 500 kW, using the fluidized-bed gasifier. In the course of works the chemical efficiency of 80% was achieved for gasification process. Gasification of wood fuel having 35% moisture content with air blow resulted in steam-air gas product with heating value of 7.4 MJ/m³. Investigation results were used at pilot mini-CHP with 200 kW capacity.

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This book aspires to be a comprehensive summary of current biofuels issues and thereby contribute to the understanding of this important topic. Readers will find themes including biofuels development efforts, their implications for the food industry, current and future biofuels crops, the successful Brazilian ethanol program, insights of the first, second, third and fourth biofuel generations, advanced biofuel production techniques, related waste treatment, emissions and environmental impacts, water consumption, produced allergens and toxins. Additionally, the biofuel policy discussion is expected to be continuing in the foreseeable future and the reading of the biofuels features dealt with in this book, are recommended for anyone interested in understanding this diverse and developing theme.

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