

SULFUR SORBENT IN COMPOSITE BRICQUETTES

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Abstract. *Basically, composite briquette comprises: biomass and tiny fractions of coal (representing fossil fuel), eventually, binding material and sulfur sorbent. In certain cases, sulfur sorbent takes over the role of binding material, as well. Composite briquette, as such, offers certain possibilities of using coals with significant contents of sulfur, in the way that SO₂ would be eliminated from the fume tract. Desulfurization process is carried out in fire-place itself, by binding of sulfur-dioxide to solid products of combustion in the form of sulfate. In their research, the authors used composite briquettes, obtained by dry and wet procedures, with calcium carbonate and lime, used as sorbents. In cases, where lime was used, it had also the function of binding material. Researches comprise as follows:*

- theoretical approach to desulfurization process;
- accompanying heat (thermal) effects in sorbent use;
- detailed description of materials applied and research methods;
- sorbent effect to briquette mechanical characteristics;
- absolute and relative desulfurization degree effects analysis and
- Ca/S molar ratio effect to desulfurization degree.

INTRODUCTION

Composite energetic briquette means a compact form, obtained by briquetting procedure of tiny matters mixture, comprising:

- basic combustion material (biomass, coals...)
- binding material and
- additives (sulfur sorbent or additives for reaching some desired effects), the basic purpose of which is to get rational heating (thermal) power quantity.

In this research, composite briquettes were investigated, obtained by:

- dry technological briquetting procedure comprising: combustion materials (wheat straw, beech sawdust and coal dust "Borovica") and calcium carbonate and calcium hydroxide as sulfur sorbents

- wet technological briquetting procedure comprising: main combustion material ("Soko" coal), binding agents (paper pulp and semi-celulose) and calcium carbonate and calcium hydroxide as sulfur sorbents.

A specific additive type in a composite briquette is sulfur sorbent, the task of which is to bind SO₂, formed during the combustion of coke residue and volatile, reducing in that way SO₂ concentration in combustion products to maximum allowed concentration.

In carried out researches, the following were used as sulfur sorbents:

- dolomite - CaCO₃ · MgCO₃,
- calcium carbonate - CaCO₃ and
- hydrated lime - Ca(OH)₂.

Sorbent share in composite briquette is manifested in the briquette itself, by effecting its:

- thickness,
- mechanical properties,
- calorific value and
- combustion process.

Sulfur dioxide elimination from the flue gas by its binding to dolomite and lime, represents a complex process, depending on sorbent physical properties (particles size, chemical nature, porosity, quantity in the fuel and reactions process conditions (SO₂, CO₂ and O₂ concentrations, temperature, pressure, calcination conditions etc.). Depending on sulfur contents within the fuel and prescribed maximum allowable SO₂ concentrations, a need will rise for dosing certain quantities of sorbent. Such quantity directly effects the economic justification of such procedures application (namely, desulfurization and composite briquettes fabrication).

1. EMPIRICAL FORMULA OF A COMPOSITE BRIQUETTE WITH SULFUR SORBENT

For the most general case, composite briquette with sulfur sorbent empirical formula would have the form as follows:



where a chemical formula of sorbent would be fixed in **SOR** place and in sor index place - sorbent molar share brought down to one mole of carbon from a combustion mixture [11].

1.1. Calcium carbonate as sulfur sorbent

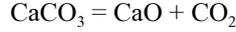
If the composite energetic briquette with a significant contents of sulfur incorporates sorbent in the form of calcium carbonate (CaCO₃), then the empirical formula would have the following form [11]:



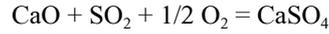
where sor (=) mol_{CaCO₃}/mol_C - molar share of sorbent is brought down to mole of carbon in the fuel.

In a theoretical case (for which full conversions of carbon to carbon dioxide and sulfur to sulfur dioxide are understood), the following presumptions would be introduced:

- at the process carrying out temperature complete calcination of incorporated sorbent would occur as per reaction



– the generated calcium-oxide would react in the sulfatization process, as well, fully binding the sulfur dioxide as per reaction:



For these reasons, theoretical quantity of oxygen defined for sorbent free fuel empirical formula the form of which is:

$$O_{\min}^M = 1 + \frac{\chi}{4} + \sigma - \frac{\Omega}{2} \quad (1)$$

must be corrected for a half of oxygen mole, engaged in the sulfatization process. Having in mind that this oxygen mole half binds one mole of sulfur dioxide that is generated on the basis of one mole of sulfur, and that in the fuel there is σ moles of sulfur, then the theoretical oxygen quantity of $\sigma/2$ moles would be necessary for sulfatization process. So, for this fuel case, the theoretical oxygen quantity amounts to:

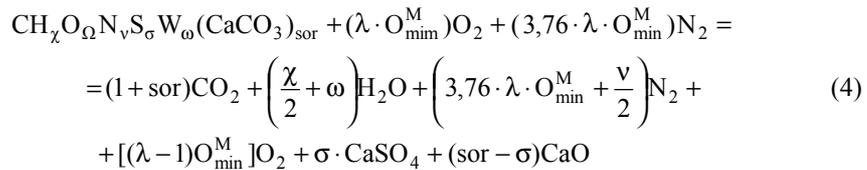
$$O_{\min}^M = 1 + \frac{\chi}{4} + \sigma - \frac{\Omega}{2} + \frac{\sigma}{2} \quad (2)$$

which, as settled, amounts to:

$$O_{\min}^M = 1 + \frac{\chi}{4} + \frac{3}{2} \cdot \sigma - \frac{\Omega}{2} \quad (3)$$

In the theoretical presumption of calcination and sulfatization, the combustion products would not contain sulfur dioxide, because it would completely be bound in sulfate, namely in the quantity of $\sigma \cdot \text{CaSO}_4$. Having in mind that a sorbent is always incorporated in the fuel in the quantity higher than theoretically necessary, the products would contain calcium oxide CaO in excess, namely in the quantity that did not react with SO_2 , and it would amount to $(\text{sor} - \sigma)$. Since in the calcination process 1 mole of CO_2 is generated from 1 mole of CaCO_3 , the products would be found to have additional quantity of $\text{sor} - \text{CO}_2$ moles of carbon-dioxide.

In that case, the solid fuel (with incorporated sorbent in the form of lime) combustion equation, has the form as follows [11]:



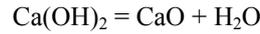
1.2. CALCIUM HYDROXIDE AS SULFUR SORBENT

Solid fuel with sulfur contents, may have hydrated lime $\text{Ca}(\text{OH})_2$, incorporated as an additive in the form of sorbent. In that case, the empirical formula would have the following form [9]:

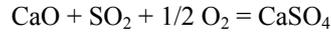


And here, as well, for a theoretical case, (for which full conversions of carbon to carbon dioxide and sulfur to sulfur dioxide are understood), the following presumptions would be introduced:

- at the process carrying out temperature, there occurs complete dehydration of the sorbent incorporated, as per reaction



- as well as in the case when calcium-carbonate is the sorbent, calcium-oxide generated would react in sulfatization process, also fully binding the generated sulfur dioxide as per reaction

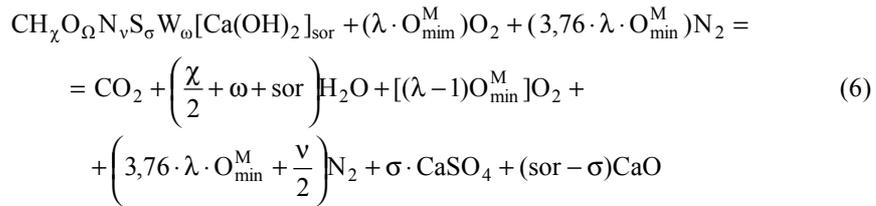


Accordingly, theoretical oxygen quantity here, is

$$\text{O}_{\text{min}}^{\text{M}} = 1 + \frac{\chi}{4} + \frac{3}{2} \cdot \sigma - \frac{\Omega}{2} \quad (5)$$

In theoretical presumption of dehydration and sulfatization in combustion products, there would not be sulfur dioxide, because it is all bound to sulfate, namely, in the quantity of $\sigma \cdot \text{CaSO}_4$. Having in mind that the sorbent is always incorporated in the fuel in the quantity higher then theoretically necessary, the products would be found to have calcium oxide CaO in excess, namely, in the quantity that did not react with SO_2 , and it amounts to $(\text{sor} - \sigma)$. Since in dehydration process, out of 1 mole of $\text{Ca}(\text{OH})_2$, 1 mole of H_2O is generated as well, consequently, the products would be found to contain additional quantity of $\text{sor} \cdot \text{H}_2\text{O}$ moles of water.

In that case, the combustion equation of solid fuel (with sorbent incorporated in the form of hydrated lime) has the form [11]:



2. COMBUSTION EQUATION AND DESULFURIZATION DEGREE (LEVEL)

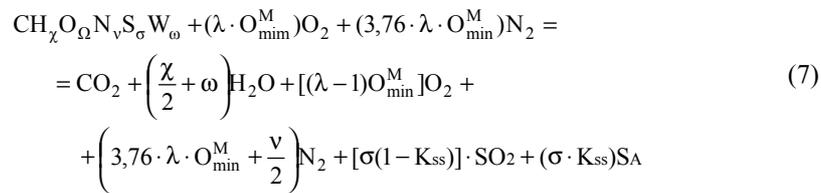
2.1. Sorbent free composite briquettes combustion equation

In normal conditions, complete contents of combustible sulfur (represented by combustible S elementary analysis data) would never be found in combustion products, in the form of SO_2 , for two reasons:

1. the process is imperfect so that the combustible sulfur complete combustion is not possible;

2. in the fuel mineral contents there is always certain quantity of natural sorbent, so that due to its presence, the so called self-desulfurization or flue gas self-desulfurization is carried out.

In that way, a part of combustible sulfur is found in ashes in the form of some compound which is not possible to define without the knowledge of naturally contained sorbent structure in the fuel mineral admixtures. If the designation, according to ash elementary analysis, is A, that is, a let the designation for sulfur, bound in the form of ash sulfate, be S_A . For such consideration, the combustion equation, taking into account self-desulfurization, has the form as follows:



where: $K_{\text{ss}} = \frac{S_{\text{svez}}}{S} \left(\frac{\text{molSvez}}{\text{mols}} \right)$.

- sulfur binding coefficient in ashes by self-desulfurization effect, representing sulfur share in the total combustible quantity that binds to solid products of combustion;

$(1 - K_{\text{ss}})$ - sulfur share, found in gaseous products;

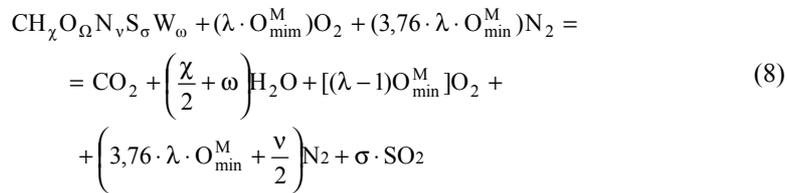
$(\sigma \cdot K_{\text{ss}}) \left(\frac{\text{molS}_A}{\text{molC}} \right)$ - sulfur molar quantity in solid products of combustion.

In such conditions, on the right side of equation sign, all the members are in gaseous aggregate state, except this, last member, that is in solid aggregate state. In that, care should be taken for symbol S_A not to represent the so called incombustible sulfate sulfur, defined by the fuel technical analysis.

In case the combustion process would not have the self-desulfurization effects, i.e., if sulfur would not be bound in the solid products of combustion, we would have:

$$\begin{aligned} S_{\text{ssvez}} &= 0 \\ K_{\text{ss}} &= 0 \end{aligned}$$

and the combustion equation would get the form:



which means that the whole available sulfur quantity σ would be converted into its oxide $(\sigma) \text{SO}_2$. Such sulfur quantity in gaseous aggregate state is equivalent to calculation quantity of possible sulfur conversion into its dioxide.

Based on combustion equations sulfur may be defined at:

– process inlet $S_u = \sigma \left(\frac{\text{mols}}{\text{molc}} \right)$ and

– process outlet S_i which, in case of full conversion into dioxid, would amount to:

$S_i = \sigma \left(\frac{\text{molSO}_2}{\text{molc}} = \frac{\text{mols}}{\text{molc}} \right)$, and in case of outlet desulfurization effect, it would be in

the quantity of $S_i^* = \sigma(1 - K_S) \left(\frac{\text{molSO}_2}{\text{molc}} = \frac{\text{mols}}{\text{molc}} \right)$ in the form of gaseous aggregate state and in the quantity of $\sigma K_{SS} \left(\frac{\text{mols}_A}{\text{molc}} \right)$ in the form of solid aggregate state.

In case there is self-desulfurization effect in briquette, with no incorporated sorbent, there may be defined the degree of absolute desulfurization of flue gas as:

$$\eta_{\text{des}}^{\text{samo}} = \frac{S_u - S_i^*}{S_u} \quad (9)$$

expressed as relative value and percentage value

$$\eta_{\text{des}}^{\text{samo}} = \frac{S_u - S_i^*}{S_u} \cdot 100 \quad (\%)$$

that, in this case, would amount to

$$\eta_{\text{des}}^{\text{samo}} = \frac{\sigma - \sigma(1 - K_{SS})}{\sigma} = K_{SS}$$

The value of absolute self-desulfurization is equal to the coefficient of sulfur binding to ash products.

2.2. Sorbent incorporated composite briquettes combustion equation

Empirical formula of sorbent incorporated composite briquettes, of the form:



no matter if the sulfur sorbent is in the form of calcium carbonate CaCO_3 or calcium hydroxide Ca(OH)_2 provides for very easy finding out the molar relation $(\text{Ca/S})^M$:

$$\left(\frac{\text{Ca}}{\text{S}} \right)^M = \frac{\text{SOR}_1}{\sigma} (=) \frac{\text{molCaCO}_3}{\text{mols}} = \frac{\text{molCa}}{\text{mols}}$$

$$\left(\frac{\text{Ca}}{\text{S}} \right)^M = \frac{\text{SOR}_2}{\sigma} (=) \frac{\text{molCa(OH)}_2}{\text{mols}} = \frac{\text{molCa}}{\text{mols}}$$

Data about the molar relation $(\text{Ca/S})^M$ are essential to evaluate the desulfurization effects and calculate the sorbent required quantity.

Theoretically:

- if there is no naturally contained sorbent in fuel mineral admixtures, for the flue gas desulfurization it should be $(Ca/S)^M = 1$,
- if there is sorbent in mineral admixtures and if the self-desulfurizing effects are present, in composite briquettes there can be established the relation $(Ca/S)^M < 1$,
- and practically, to achieve desulfurizing effect, there should always be $(Ca/S)^M > 1$.

In case of incorporated sorbent with molar relation $(Ca/S)^M > 1$, when the sorbent is $CaCO_3$ in the combustion products, apart from customary products, there would be found carbon dioxide, calcium oxide, and calcium sulfate, as products of calcination and sulfatization.

If, for the incorporated sorbents composite briquettes combustion process, it is presumed that:

- combustion is carried out with excess air coefficient $\lambda > 1$;
- molar relation is $(Ca/S)^M > 1$;
- all carbonate is subject to calcination;
- all generated SO_2 takes part in sulfatization process, building up $CaSO_4$; and in that, moisture is transformed in water steam and hydrogen combusts into product (water), that is also going to be in the form of steam so as not to react with calcium oxide;
- in mineral admixtures there are no admixtures of forced sorbent nor the effects of self-desulfurization

then the combustion equation would have the following form (4).

In such description of combustion process, sulfatization and calcination in one common equation – equation of collective effect, the two last members on the right side of the equation mark are in solid aggregate state, while the other members represent gaseous combustion products.

In that case the absolute level (degree) of flue gas desulfurization may be defined as

$$\eta_{des}^A = \frac{S_u - S_i}{S_u}$$

$$\eta_{des}^A = \frac{\sigma - O}{\sigma} = 1$$

which means that it is maximum (100%) because there is no sulfur in gaseous products at all.

In real conditions, however, due to imperfection of combustion process and sulfatization process, there is always certain quantity of SO_2 in combustion gaseous products, regardless of self-desulfurization and forced desulfurization effects, owing to additives in capacity of sorbent.

Therefore, combustible sulfur, entering the S process, after the completed combustion process, would be found in certain quantities in:

- gaseous combustion products S_{gp} ,
- bound in sulfate compounds by self-desulfurization processes S_{Svez} and
- (force) bound in sulfate compounds by means of added sorbent S_{Pvez} ,

so that:

$$S = S_{dg} + S_{Svez} + S_{Pvez}$$

that is:

$$1 = \frac{S_{dg}}{S} + \frac{S_{Svez}}{S} + \frac{S_{Pvez}}{S}$$

$$1 = \frac{S_{dg}}{S} + K_{SS} + K_{PS}$$

where:

$K_{SS} = \frac{S_{Svez}}{S}$ - is sulfur binding coefficient in solid products by self-sulfurization effects

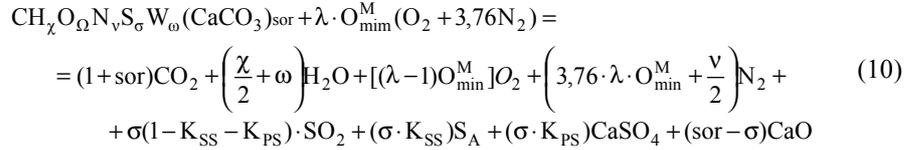
$K_{PS} = \frac{S_{Pvez}}{S}$ - is sulfur binding coefficient in solid products by added sorbent sulfatization effects.

So, the sulfur share to be found in flue gas would be defined by expression:

$$\frac{S_{dg}}{S} = 1 - K_{SS} - K_{PS}$$

from which it could be seen that it equals one, reduced for self-sulfatization K_{SS} and forced sulfatization K_{PS} coefficients.

Now, the equation describing combustion process, sulfatization and calcination for $\lambda > 1$, $(C_A/S)^M > 1$ of the present natural and forced sulfatization, may be written in the form:



In this equation, on the product side, i.e., on the right side of equation mark, the last three members represent solid aggregate state, therefore, the absolute degree of flue gas desulfurization may be defined as:

$$\eta_{des}^A = \frac{S_u - S_i}{S_u} = \frac{\sigma - \sigma(1 - K_{SS} - K_{PS})}{\sigma} = K_{SS} + K_{PS} \quad (11)$$

that is, the sum of binding coefficients into solid products by means of self-sulfatization and forced sulfatization processes. It is confirmed by coefficients in solid stage of products that bound sulfur.

From the expression derived it can be seen that the absolute desulfurization degree comprises one constant part – due to sorbent present in mineral admixtures and other relative part – being the effect of forced dosed sorbent:

$$\eta_{des}^A = \eta_{des}^{samo} + \eta_{des}^R \quad (12)$$

η_{des}^{samo} - self-desulfurization degree

η_{des}^R - relative desulfurization degree which is the result of dosed sorbent with particular molar ratio (Ca/S).

Starting from the set definition of absolute desulfurization degree (11) and (9), by including it in (12)

$$\frac{S_u - S_i}{S_u} = \frac{S_u - S_i^*}{S_u} + \eta_{des}^R$$

and by its arranging

$$\eta_{des}^R = \frac{S_i^* - S_i}{S_u} \quad (13)$$

a definition of relative desulfurization degree is reached which represent the quantity of bound sulfur by forced added sorbent into the composite briquette (expression 13).

On the other hand, based on the expression (13) – it represents the difference of sulfur combustion process outlet quantity, established in self-desulfurization effect (S^*) and sulfur quantity established at the inlet with the added sorbent having corresponding molar ratio $(C_A/S)^M$, brought down to the sulfur quantity entering the combustion process.

3. POSSIBILITY OF ESTABLISHING DESULFURIZATION DEGREE

The possibilities of establishing absolute and relative desulfurization as well as self-desulfurization degrees are based on determination of sulfur contents at the combustion process outlet and inlet, and these are S_u , S_i^* and S_i values. Practically, it is possible to determine actual sulfur state at the outlet of S_i or S_i^* processes by corresponding gas analyzers or other measuring instruments, in the way that sulfur dioxide concentrations are usually measured in the following measurement units:

$$\frac{\text{mgSO}_2}{\text{m}_{sg}^3} = \frac{10^{-3} \text{gSO}_2}{\text{m}_{sg}^3} = 3,502 \cdot 10^{-7} \frac{\text{m}_{so_2}^3}{\text{m}_{sg}^3} \quad \text{or} \quad \text{ppmSO}_2 = 10^{-6} \frac{\text{m}_{so_2}^3}{\text{m}_{sg}^3} \quad (14)$$

where sg indexes indicate the fact that SO_2 in gaseous products is brought down to dry gas, as established by gas analyzers.

On the other hand the sulfur quantity at the process inlet S_u is the one that corresponds to elementary analysis and which was incorporated, by corresponding mathematical operations, in an empirical formula, designed as σ (mols / molC).

In order to be brought down to dry products, as was done with S_i , the data should be used to indicate that dry gaseous combustion products total number of moles is:

$$N_{SP} = (1 + \text{sor}) + (\lambda - 1)O_{\min}^M + \left(3,76 \cdot \lambda \cdot O_{\min}^M + \frac{v}{2} \right) + \sigma \left(\frac{\text{molSP}}{\text{molC}} \right) \quad (15)$$

obtaining in that way the sulfur quantity at the process inlet, brought down to dry products as:

$$S_U = \frac{\sigma \left(\frac{\text{mols}}{\text{molC}} \right)}{N_{SP} \left(\frac{\text{molSP}}{\text{molC}} \right)} (=) \left(\frac{\text{mols}}{\text{molSP}} \right) \quad (16)$$

Application of such an expression to calculate the quantities of dry combustion products may result in a certain error, because with this expression:

- on one hand, CO_2 quantity generated by carbonate dissolution, is not taken into consideration

- on the other hand, total SO₂ quantity is taken into consideration, as generated by complete sulfur combustion.

However, from the equations given, (for self-desulfurization and forced desulfurization effects), it can be seen that the expression for dry products quantity looks different.

For a more precise algorithm of desulfurization effects calculation, the following data should be introduced in calculations:

- sorbent (lime) purity coefficient and CaCO₃ share in it;
- calculation of CO₂ partial pressure and calcination process state of balance;
- method to define more closely the conversion degree into sulfate CaSO₄;
- CaO behavior in relation to the generated water steam.

Model without these presumptions, but with using expressions (12), (13) i (15), has been adopted as a simplified model to view desulfurization process.

4. SULFUR SORBENT COMPOSITE BRIQUETTES CALORIFIC VALUE

Calorific value, the most important data in composite briquettes technical analysis, depends not only on combustible mass combustion heat, but on heat effects of additives, sorbent in the first place. To calculate the calorific value of coals in a calorimeter with a bomb, we use the expression:

$$H_S = Q_B + \sum \Delta Q$$

where: $\sum \Delta Q = -\Delta Q_{H_2SO_4} - \Delta Q_{HNO_3}$,

$\Delta Q_{H_2SO_4}$ - heat effect of sulfuric acid formation (generation),

ΔQ_{HNO_3} - thermal effect of nitric acid formation and

Q_B - heat effect of the basic combustible material without correction.

A more precise expression for defining composite briquettes calorific value may be formed by adding members that also take into account the heat effects of carbon incomplete combustion, carbonate incomplete decomposition, as well as the heat effects of natural sulfur and sulfates generation. When it is to do with mineral structured binders based on marl or clay forms structure, it is also necessary to take into consideration the heat effects of crystalline moisture elimination.

One of more simplified expressions for defining composite briquettes combustion heat in a calorimeter with a bomb is:

$$H_S = Q_B + \sum \Delta Q$$

in that: $\sum \Delta Q = \Delta Q_G - \Delta Q_{H_2SO_4} + \Delta Q_S - \Delta Q_K - \Delta Q_{HNO_3} + \Delta Q_{Sp}$

where: ΔQ_G - heat effect of carbon incomplete combustion,

$\Delta Q_{H_2SO_4}$ - heat effect of SO₃ dissolution in water,

ΔQ_{Sp} - heat effect of iron disulfide sulfur incomplete combustion,

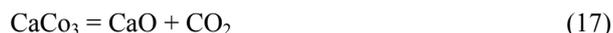
ΔQ_S - heat effect of sulfate formation,

ΔQ_K - heat effect of carbonate incomplete decomposition and

ΔQ_{HNO_3} - heat effect of nitric acid formation.

4.1. Calcination process

After dolomite or lime particles are introduced in the combustion process, these are subject to heating and calcination. The results of that are considered to be the increase of particles pores diameter and porosity and particles active surface increase. Calcination process:



is endothermic and its reaction heat at the temperature of process carrying out T , may be calculated from the expression :

$$\Delta H_{rT} = -1,00089 \cdot C_{PCaCO_3}(T - 298) + 182600 + 0,05608 C_{PCaO}(T - 298) + i_{rCO_2} \quad (18)$$

where:

- C_{PCaCO_3} i C_{PCaO} (J/kgK) - is the heat capacity of lime and calcium oxide (it may be taken as 840 J/kgK),
- i_{rCO_2} (J/mol) - enthalpy of carbon dioxide at the combustion process carrying out temperature and
- 182600 (J/mol) - calcination reaction standard heat.

In most mathematical procedures it is understood that the sorbent is perfectly mixed in composite briquettes owing to good mixing and long time of its remaining in the fire place and that the temperature in the layer is even. Basically, this presumption is correct, except in case when the partial CO_2 pressure equals the pressure corresponding the balance (equilibrium) state. For that reason, it is necessary to know the equilibrium state gaseous component partial pressure at the combustion process temperature, i.e., calcination reaction, in order to be able to estimate the calcination degree.

It is outlined, however, that the effect of the reaction gaseous product, (i.e., the degree of reaction moving away from the equilibrium state) to the activation energy value has a wider effect and it need not be related to reversible reactions only. In such a way, it has been shown that the activation energy E depends on the reaction gaseous product in heat decomposition of CaCO_3 , in the form of table contained values (table 4.1):

Table 4.1. E dependence from P_{CO_2} in heat decomposition of CaCO_3 [10]

$P_{CO_2} \cdot 10^{-2}$ (kJ/mol)	1,33	6,65	13,30	26,6	39,9	59,85
E (Pa)	186,20	290,40	390,40	576,6	629,7	1535,5

On the other hand, activation energy E and pre-exponential factor K_0 in Arenius' law, depend on carbonate origin that can be seen from the table 4.2.

Table 4.2. Kinetic parameters values in heat decomposition of CaCO_3 of various origin [10]

Origin CaCO_3	E (kJ/mol)	K_0
From the marble	149,8	1,65 E 08
From calcite	157,3	3,16 E 08
CaCO_3	158,2	7,65 E 08
From oxalate	183,3	6,66 E 09
From dolomite 5	217,1	2,94 E 11
From dolomite 6	233,9	2,15 E 12

4.2. Sulfatization process

After the calcination process is carried out, sulfur dioxide of the layer **releases** through the pores and reacts with calcium oxide, forming calcium sulfate in that way. Since the molecular volume of this product is voluminous, related to the basic reactant, it results in pores clogging, the particle effective surface reduction and significant speed decrease before the whole sorbent particle starts reacting.

Sulfatization process is carried out according to **stoichiometrical** equation:



This reaction is usually considered to be of the first order, related to SO_2 and of zero order, related to O_2 . It has exothermic character and the reaction heat at the process carrying out temperature may be calculated according to the expression:

$$\Delta H_{RT} = -[0,05608C_{\text{PCaO}}(T - 298) + i_{\text{TSO}_2} + \frac{1}{2}i_{\text{TO}_2}] - 484900 + 0,13614 \cdot C_{\text{PCaSO}_4}(T - 298) \quad (20)$$

where:

- C_{PCaO} and C_{PCaSO_4} (J/kgK) - Calcium oxide and calcium phosphate heat capacity,
- i_{TSO_2} and i_{TO_2} (J/mol) - sulfur oxide and oxygen enthalpy at the layer temperature and
- 484900 (J/mol) - standard sulfatization reaction heat.

Sulfatization process reaction heat value reduces calcination heat losses to a certain extent, and the actual values, depend on temperature conditions and sorbent dosing quantity.

The pores clogging process, due to gypsum formation brings about the progressive decrease of CaO particle active surface, so that generally accepted way for showing that dependence is in exponential form. However, having in mind that this problem exceeds the scope of this work, it would not be studied further.

Note: Sulfatization and calcination processes heat effects were treated here, the way the chemists do, so that the value for ΔH_R of calcination + (182600 J/mol) is as given for endothermic reaction and for ΔH_R of sulfatization -484900 J/mol is given as for exothermic reaction.

4.3. Enthalpies of products and reactants in sulfatization and calcination processes

For the needs of described reactions mathematical modelling, the authors suggest their tested and evaluated expressions for combustion gaseous products enthalpies calculations.

Molar enthalpies may be calculated in the polynome form of second order as:

$$i_i^M = a_0 + a_1 \cdot T + a_2 \cdot T^2 \quad [\text{J/mol}] \quad (21)$$

where:

- i_i^M [J/mol] - molar enthalpy of i - component in combustion products,
- a_0, a_1, a_2 - coefficients and
- T [K] - temperature.

Meaning of suffixes and indexes to basic designation of enthalpy i :

- index comprises chemical designations of combustion products components,
- index L was adopted for air (German word - Luft) and
- suffix M designates molar enthalpy [J/mol].

Molar enthalpies for individual components in combustion products based on equation (21) [7]:

$$\begin{aligned}
 i_{\text{CO}_2}^{\text{M}} &= -16\,014,60 + 47,8140 \cdot T + 0,0029557 \cdot T^2 \\
 i_{\text{CO}}^{\text{M}} &= -8\,436,93 + 29,4241 \cdot T + 0,0016734 \cdot T^2 \\
 i_{\text{H}_2\text{O}}^{\text{M}} &= -10\,601,50 + 34,1099 \cdot T + 0,0039693 \cdot T^2 \\
 i_{\text{NO}_2}^{\text{M}} &= -10\,359,80 + 32,5855 \cdot T + 0,0009427 \cdot T^2 \\
 i_{\text{O}_2}^{\text{M}} &= -7\,554,44 + 26,3803 \cdot T + 0,0047361 \cdot T^2 \\
 i_{\text{SO}_2}^{\text{M}} &= -15\,138,20 + 48,8610 \cdot T + 0,0020439 \cdot T^2 \\
 i_{\text{N}_2}^{\text{M}} &= -10\,359,8 + 32,5855 \cdot T + 0,0009427 \cdot T^2 \\
 i_{\text{L}}^{\text{M}} &= -7\,805,67 + 28,1545 \cdot T + 0,0015450 \cdot T^2
 \end{aligned}$$

For more precise calculations, molar enthalpies may be used in the form of third order polynome, as:

$$i_i^{\text{M}} = a_0 + a_1 \cdot T + a_2 \cdot T^2 + a_3 \cdot T^3 \text{ [J/mol]} \quad (22)$$

where:

i_i^{M} [J/mol] - molar enthalpy of i - component in combustion products

a_0, a_1, a_2, a_3 - coefficients

T [K] - temperature

Molar enthalpies for individual components in combustion products based on equation (22) [7]:

$$\begin{aligned}
 i_{\text{CO}_2}^{\text{M}} &= -737,12 + 15,0717 \cdot T + 0,02293240 \cdot T^2 - 3,6257 \cdot 10^{-6} T^3 \\
 i_{\text{CO}}^{\text{M}} &= -10\,075,70 + 31,5954 \cdot T + 0,00107112 \cdot T^2 + 3,7078 \cdot 10^{-15} T^3 \\
 i_{\text{H}_2\text{O}}^{\text{M}} &= -5\,848,30 + 22,5407 \cdot T + 0,00114655 \cdot T^2 - 1,4036 \cdot 10^{-6} T^3 \\
 i_{\text{NO}_2}^{\text{M}} &= -16\,116,30 + 47,5959 \cdot T + 0,00192798 \cdot T^2 - 1,6005 \cdot 10^{-31} T^3 \\
 i_{\text{O}_2}^{\text{M}} &= -9\,834,20 + 32,3126 \cdot T + 0,00127777 \cdot T^2 - 9,2963 \cdot 10^{-15} T^3 \\
 i_{\text{SO}_2}^{\text{M}} &= -11\,231,10 + 37,5906 \cdot T + 0,01028400 \cdot T^2 - 1,6243 \cdot 10^{-6} T^3 \\
 i_{\text{N}_2}^{\text{M}} &= 5\,298,62 + 0,0120 \cdot T + 0,01932140 \cdot T^2 - 3,1866 \cdot 10^{-6} T^3 \\
 i_{\text{L}}^{\text{M}} &= -7\,914,06 + 29,0713 \cdot T - 0,00097337 \cdot T^2 + 2,2506 \cdot 10^{-6} T^3
 \end{aligned}$$

Regarding the kind of phase, either in products or in reactants (CaCO_3 ; CaO ; CaSO_4) it can be calculated through the expression $C_p (T - T_0)$, where $C_p \approx 840 \text{ J/kgK}$ their heat capacity, $T_0 = 298 \text{ K}$, and $T(\text{K})$ is the temperature of the process considered.

5. MATERIAL AND METHOD

5.1. Material

We investigated composite briquettes, composed of: combustible material, binding material and additives.

Combustible materials used were:

- beech tree sawdust
- wheat straw
- coaldust "Soko" and
- coaldust "Borovica"

Binding materials were:

- paper pulp and
- semi-cellulose

Sorbents:

- calciumcarbonate and
- hydrated lime

• **Beech sawdust**

Beech (*Fagus silvatica* L.) High and beautiful tree, with dense and big treetop, that can grow up to 30 meters height, usually spread in high mountain areas, in deciduous or mixed woods (most frequently with fir trees). Apart from oak, it is the tree, most frequently found in our country, used as technical and heating tree.

Basic characteristics, granulation, moisture contents, bulk mass volume, composition of elements and a part of technical analysis of sawdust are given in tables 5.1, 5.2 and 5.3.

Table 5.1. Physical properties beech sawdust [9]

Biomass	Bulk mass volume (kg/m ³)	Moisture contents (%)	Granulation (mm)	State of measurement
Beech - sawdust	169	6,675	0 - 2	left-overs after cutting

Table 5.2. Elements composition and part of beech sawdust technical analysis [9]

Biomass	Vols	Cfix	Cs	Hs	Ss	Ns	As	Os
Beech - sawdust	85,03	13,86	50,46	6,01	0,01	0,16	1,11	42,25

Table 5.3. Beech sawdust technical analysis [9]

Biomass	WHa (%)	Aa (%)	Vola (%)	Cfix a (%)	Coke residue (%)	Combust. (%)	Hg a (MJ/kg)	Hd a (MJ/kg)
Beech - sawdust	6,675	1,688	70,70	20,937	22,625	91,637	16,567	15,151

• **Wheat straw**

Wheat belongs to grass family (GRAMINACEAE) and sub-family Hordeae. That is an one year plant, originating from South-West Asia, used as the most important bread wheat in Europe, North America and Oceania. Almost 40% of the world population is fed

by it. Wheat is the culture of moderate zone. It gives very good harvests in continental climate steppe fertile soils.

Physical properties of wheat straw and wheat straw biobriquettes are shown in Tables 5.4. and 5.5, and elements composition and technical analysis data in Tables 5.6. i 5.7.

Table 5.4. Wheat straw physical properties [9]

Biomass	Bulk-volume mass (kg/m ³)	Moisture contents (%)	State of measurement
Wheat straw	24	6,214	natural size in left-overs without pressure

Tabela 5.5. Wheat straw biobriquettes physical properties [9]

Biomass	Volumenous masses			Characteristics			
	Bulk-volume			B	K _b	K _{sb}	η _{sb}
	biomass	biobriquette	biobriquette				
	kg/m ₃	kg/m ₃	kg/m ₃	–	–	–	(%)
Wheat straw	24	390	1015	0,384	42,3	0,062	93,8

Table 5.6. Technical analyses of biomasses investigated [9]

No	Sample	W _{H(a)} (%)	A _(a) (%)	Vol _a (%)	C _{fix(a)} (%)	Coke residue(%)	Combust. (%)	H _{g(a)} (MJ/kg)	H _{d(a)} (MJ/kg)
1	Wheat straw	6,214	5,549	75,37	12,867	18,416	88,24	16,650	15,357

Tabela 5.7. Some biomasses elements composition (brought down to combustible mass), as well as some data for analytical samples [9]

Elem. composit.	C _g (%)	H _g (%)	S _g (%)	N _g (%)	O _g (%)
–	46,78	5,73	0,10	0,52	46,78
–	49,87	6,21	0,17	1,5	42,24

• Coal dust "Soko"

Elements composition and technical analysis data are shown in Table.5.8, and the result of constituent analysis, in Figure 5.1.

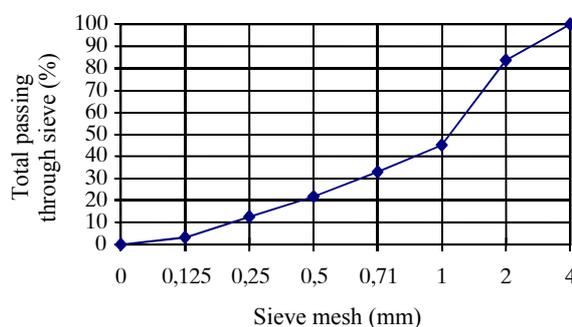


Fig. 5.1. Coal dust "Soko" sieve analysis [5]

Table 5.8. Tabular view of coal composition (dark-lignite coal Soko) containing the results of elemental and thermal (heat) analysis [5]

Technical analysis	Operating mass	Analytical mass	Absolutely dry mass	Pure combustible mass
moisture (%)	24,10	10,50	–	–
ashes (%)	27,47	32,39	36,19	–
total sulfur (%)	1,74	2,06	2,30	–
sulfur in ashes (%)	0,71	0,84	0,94	–
combustible sulfur (%)	1,03	1,22	1,36	2,14
coke (%)	48,71	57,44	64,18	43,86
fixed carbon (%)	21,24	25,05	27,99	43,86
combustible volatile matters (volatiles)	27,19	32,06	35,82	56,14
totally combustible (%)	48,43	57,11	63,81	100,00
calorific value				
fuel max. calorific value (kJ/kg)	12930	12250	17050	26700
fuel min. calorific value (kJ/kg)	11690	14230	16200	31500
Elements analysis	Operating mass	Analytical mass	Absolutely dry mass	Pure combustible mass
total carbon (%)	32,44	38,25	42,74	66,98
hydrogen (%)	2,86	3,37	3,76	5,90
combustible sulfur (%)	1,03	1,22	1,36	2,15
nitrogen and oxygen (%)	12,10	13,87	15,95	24,98
moisture (%)	24,10	10,50	–	–
ashes (%)	27,47	32,39	36,19	–

• Coal dust "Borovica"

Coal dust sample was obtained from the coal that belongs to the class of dark lignite coals of "Borovica" mine – Pljevlja coal basin.

Coal of this mine has a low calorific value (6200 kJ/kg – 11200 kJ/kg). For preparation of coal dust, we took the coal of regular production, from conveyer, after crushing. Coal dust was obtained from the UG-90 crusher (stroke granulator-hammer), the capacity of which is 500 t/h with cyclone dedusting of incoming granulation of 800 – 900 mm and outcoming of 30–50 mm [5].

Crushed coal of 30–50 mm granulation was dried at room temperature, at that lost rough moisture (24%) and then, ground in laboratory mill that works on clearing plates principle, with fineness of milling material to pass the sieve of 0.2 mm size (900 openings/cm²).

• Calcium hydroxide

Sorbent component in the form of hydrated lime Ca(OH)₂ originates from trade and it is used for various commercial needs. This component has also got the role of sulfur sorbent in the combustion process

• Paper pulp

The Table 5.9. shows elements analysis of various kinds of papers (pure combustible mass). It can be seen that the newspaper paper has the highest percentage of carbon and the lowest of sulfur.

Table 5.9. Elemental analysis of various kinds of paper (solid combustible mass) as compounds componenat [5]

No.	Component description	C ^g (%)	H ^g (%)	O ^g (%)	N ^g (%)	Cl ^g (%)	S ^g (%)	Σ (%)
1	Coated paper	47,33	6,53	45,55	0,14	0,15	0,30	100,00
2	Newspaper paper	49,86	6,34	43,24	0,15	0,15	0,26	100,00
3	Books, magazines	46,46	6,55	46,35	0,16	0,18	0,30	100,00
4	Other kinds of paper	47,70	6,64	44,02	0,46	0,90	0,28	100,00

Paper pulp may be obtained from waste paper, after its submerging in water basins, where after the long enough period of stay, its fibers are separated. Such a raw material is used in paper and card industry, although it may serve as binding means in wet briquetting procedures. In the paper industry, one part of the liquid coming from the process of fibers separation is passed to sewerage as sludge. Depending on technological level, this sludge contains certain quantity of fibers that can range up to 60%.

• Semi-cellulose

According to chemical composition, cellulose stands between wood and cellulose. Unlike cellulose obtaining process when it is desired to separate cellulose accompanying products (lignin and hemi-cellulose) as much as possible, in semi-cellulose obtaining process, the process is interrupted before lignin and hemi-cellulose are fully separated. To put it in other words, the process is interrupted when the wood chemical structure is loose enough to facilitate fibers separation.

As the raw material for semi-cellulose production deciduous woods are used. Having in mind shorter contact with chemicals in the production process, semi-cellulose fibres have greater strength than cellulose fibers.

• Calcium carbonate "Visocica"

Carbonate flour is produced from stone of the quarry "Visocica", by customary lime obtaining process. By grinding process, lime flour - filler is obtained, of 5 – 10 microns granulation CaO - 55,1%, SiO₂ - 0,01% [5].

• Calcium carbonate "Ostrovica"

Sorbent in the form of lime (CaCO₃) originates from lime and non-metal industry "Ostrovica", and has the role of sulfur sorbent in the combustion process. Granulation of ther used calcium-carbonate ranges from 0 to 2,5 mm, with maximum sieve residue of around 50% for the sieve mesh size of 0,71-1,0 mm (Fig. 5.2.).

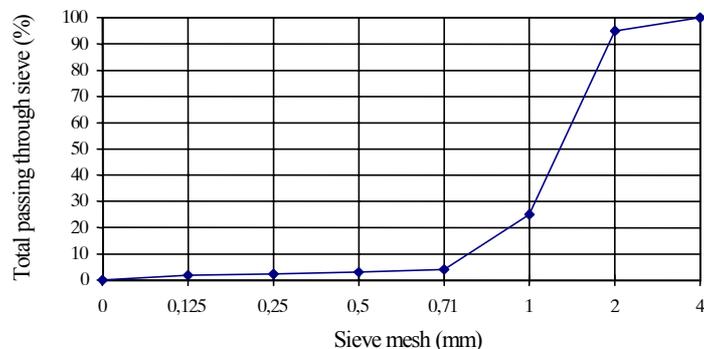


Fig. 5.2. Sieve analysis of lime from lime and non-metal industry "Ostrovnica" [5]

Physical properties and chemical composition are given in the Table 5.10.

Table 5.10. Physical and chemical properties of "Ostrovnica" lime

Description	Grey, grey-white and yellowish stone, compact and homogenous									
Purity	149 [MPa]									
Wear resistance	17,26 [cm ³ /50cm ³]									
Water absorption	0,18									
Stable at increased temperatures										
Volume mass	2,68 g/cm ³									
with pores	2,71 g/cm ³									
without pores										
Chemical composition										
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CO ₂	SO ₃	
0,44	0,18	0,19	0,48	54,61	0,42	0,06	0,01	43,59	0,07	

5.2. Production method

• Laboratory press

Technical and technological possibilities of briquetting have been tested on laboratory press (designed by D. Mitić) [6,8].

Manual laboratory press for briquettes making is of steel welded structure with two steel columns (1) of ϕ 30 mm diameter that also serves the purpose of supporting (2), tools upper part (3) and as a guide of mobile support (4) comprising tools lower part (5) for briquetting.

Briquettes making tools provide for producing cylindrical briquettes of ϕ 16 mm, ϕ 20 mm, ϕ 35 mm, ϕ 43 mm, ϕ 50 mm and ϕ 82,5 mm diameters. Non-perforated tools are intended for briquettes making by means of dry procedure and those perforated, by means of wet procedure. Cylindrical tools are made of steel with closed matrix type and conical tools are made of steel with open matrix type.

Basic press dimensions are:

- operating height - 760 mm,
- total height - 1050 mm,

- slides span - 250 mm,
- press operating width - 120 mm,
- press total width - 450 mm,
- maximum hand force - 0,5 kN.

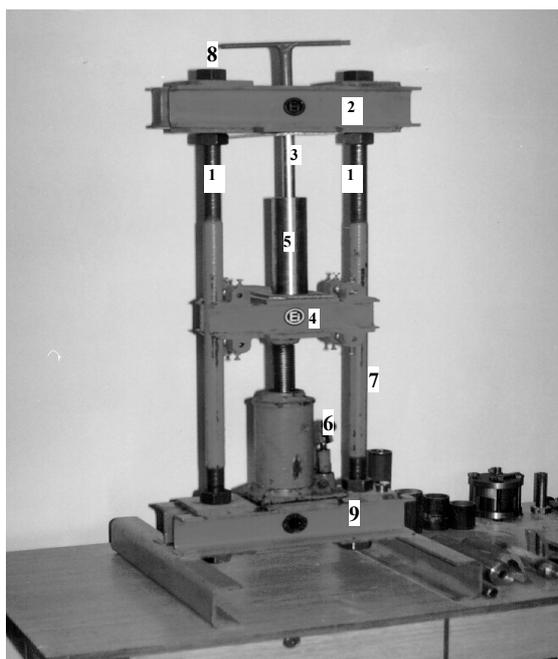
Press view is represented in Fig. 5.3.

The necessary briquetting pressure is obtained by hydraulic lift (6) hand driven (7). During the briquetting, the pressure is measured on the hydraulic cylinder piston (8) of $\phi 63$ mm diameter, by means of manometer, and the pressure of briquettes forming is calculated according to expression:

$$p_{br} = 0,1 \cdot p_M \cdot \left(\frac{d_{kl}}{d_{al}} \right)^2 \quad [\text{MP}_a]$$

where:

- p_{br} [MPa] - briquettes forming pressure,
- p_M [bar] - manometer read pressure, i.e., pressure on the hydraulic cylinder piston,
- $d_{kl} = 63$ mm - hydraulic cylinder piston diameter and
- d_{al} [mm] - tools "male" part diameter.



- | | |
|-----------------------------------|-----------------------------|
| 1. two steel columns $\phi 30$ mm | 6. manual lift |
| 2. support | 7. manual lift handle |
| 3. tools upper part | 8. connection for manometer |
| 4. mobile support | 9. base |
| 5. tools lower part | |

Fig. 5.3. View of laboratory manual press with briquettes making tools $\phi 20$ mm (photo D. Mitic)

It is possible to achieve maximum pressure on the press, at the point of “male” part effecting the material, by means of manual force $F_R = 0,5 \text{ kN}$

Tools set used in experimental work are shown in Figure 5.4.



Fig. 5.4. Tools for dry and wet briquetting procedures used in Combustion laboratory at the Faculty of Occupational Safety in Nis (design D.Mitic, photo "Inkoplan", Nis), from the left to the right:

1. extrusion hydraulic press tools for pallets making $d = 9 \text{ mm}$
2. perforated matrix tools for dry briquetting procedures $d = 82 \text{ mm}$
3. perforated matrix tools for wet briquetting procedures $d = 35,25 \text{ mm}$
4. charge filling tools with closed matrix $d = 20 \text{ mm}$
5. charge filling tools with closed matrix $d = 16 \text{ mm}$
6. charge filling tools with closed matrix $d = 22,5 \text{ mm}$
7. conical tools with open matrix $d = 50 \text{ mm}$ and the cone angle $\alpha = 1,527^\circ$
8. conical tools with open matrix $d_1 = 75 \text{ mm}$, $d_2 = 42 \text{ mm}$ and the cone angle $\alpha = 14,92^\circ$
9. conical tools with open matrix $d_1 = 65 \text{ mm}$, $d_2 = 45 \text{ mm}$ and the cone angle $\alpha = 9,2^\circ$

Achieving of such high values of surface pressures enables experiments with minimum cutting of biomass material samples into small pieces. In that way the conditions were created for heavy briquettes forming by means of high pressures up to 3000 bar (from forest branches and orchard trees branches, as well as vine and raspberry trimmings) without previous cutting into small pieces. On the other hand, forming of light briquettes has also been provided for.

So, during the experiments, surface pressures on ‘male’ part and briquetting material contact surfaces have been achieved for:

- biomass, coal and biomass and coal mixture with binding material by wet procedure up to 0,5 MPa,

- prepared biomass, coal and biomass and coal mixture of up to 3 mm granulate, with binding agent by dry procedure up to 20 MPa and
- non-prepared biomass, coal and biomass and coal mixture of up to 30 mm granulate without binding agent by means of dry procedure up to 300 MPa.

Commercial press SPANEX SHB 50

One part of experimental research was done on commercial machine – press for sawdust briquetting SPANEX SHB 50 type. On this machine, exclusively the dry-procedure of briquetting was used, namely, of sawdust / coal dust solitary and composite types.

Briquetting procedure in this hydraulic press has been carried out without additional binding materials. Hydraulic press has the electric motor power of 7,5 kW, 380 V, 50 Hz, that moves the impellers for sawdust bringing into the pressing canal. The tank for raw material is filled manually and until the tank cover is open, the press is switched off (regulated by micro-switch). After the tank has been filled with briquetting raw material, the press is started by pressing the main switch. At that, the electric motor is started and by the impellers movement, the raw material is brought to the process canal (material feed canal). At the same time, with starting of electric motor and impellers, the hydraulic pump switch is activated.

By means of a special switch on the press **RT** the choice of optimum briquette quality is made (1,2,3 circuit-breaker positions), and these are selected according to briquetting material quality (dry, tiny, etc.). When the mass has been prepared for work, automatic operation takes place. Automatic operation is ensured through a circuit breaker providing for choice of briquette optimum quality, and at the same time assigning parameters for separating certain quantity of material to fill the press chamber, in order to get the optimum briquette. In case of fine sawdust and dust mixture for cubic mass 180-200 kg/m³ – circuit-breaker position 1, for coarser voluminous materials with cubic mass 50-80 kg/m³ - position 3.



Fig. 5.5. Commercial press SPANEX SHB 50 type K2 [5]

Hydraulic press has two cylinders, one cylinder with its piston serves for accepting certain (exactly assigned by circuit-breaker position) raw material quantity and its passing

to the second cylinder. In the second cylinder – main briquette extrusion cylinder, by applying pressure of 200-220 bar (in the body it was calibrated to 280 bar) a briquette of corresponding characteristics is formed. It is only when the calibrated pressure of 200-220 bar has been achieved, that the main cylinder is opened and the briquette is finished. According to the tools – cylinder type, the corresponding form of briquette is obtained.

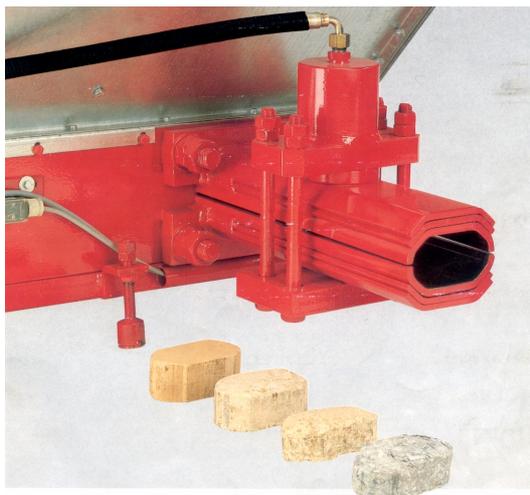


Fig. 5.6. Press SPANEX SHB 50 type K2 jaws for briquettes exit [5]

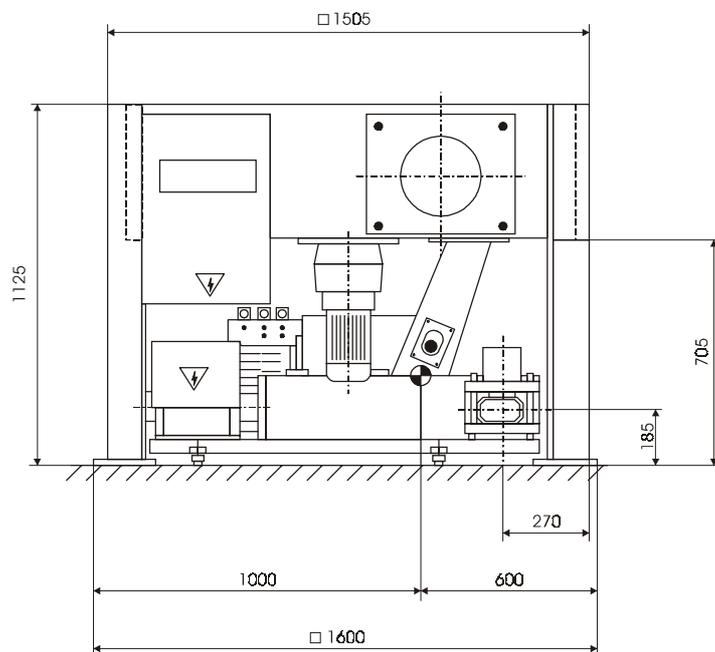


Fig. 5.7. Side view and measuring sketch of SPANEX SHB 50 type K2 press

5.3. MECHANICAL CHARACTERISTICS TESTING METHOD

Missing the adequate standards for biobricquettes testing, JUS B. H8. 376 / 82 and Proposal of Yugoslav standard JUS G S2 813 / 90 have been applied for briquettes testing to define the briquettes and pallets strength, viewed from pressure side [1,2].

The procedure is based on positioning of the test bar – briquette between the two plates of the compression testing machine. During the test, the plates move at constant speed so that the pressure onto the briquette is evenly increased. Maximum pressure of crushing (briquet destruction) is recorded.

For each briquette type, the set of 7 briquettes is taken and maximum pressure measured.

$$p_{\max} = \frac{\sum p_{\max_i}}{n} \text{ [MPa]}$$

where:

- p_{\max} [MPa] - briquette strength according to pressure
- $\sum p_{\max_i}$ [MPa] - sum of maximum pressures causing briquettes crushing and
- n - number of tested pieces

This procedure was carried out at the Faculty of Occupational Safety - Combustion laboratory press, adapted for this test (Fig. 5.8). Briquette is positioned between two plates, with pressure evenly increased afterwards. The average initial length of biobriquette was around 100 mm. During the test, the pressure in the hydraulic system was measured and recalculated to pressure obtained at the briquette surface.

During the test, not a single briquette was destroyed, but only underwent some plastic and elastic deformations. The maximum pressure taken, was the one causing first cracks on a briquette.



Fig. 5.8. Press for briquettes pressure resistance test (photo: "Inkoplan", Nis)

5.4. DESULFURIZATION PROCESS TEST METHOD

Experimental fire place

Experimental works of briquetting, combustion and experimental results processing have been done in Faculty of Occupational Safety - Combustion laboratory in Nis. The material used in this research was in the form of basically developed biobriquettes types and practically it can be defined through four types as follows:

1. heavy biobriquettes without binding materials used (samples series 301 - 311),
2. biobriquettes with paper pulp as binding material (samples series 101 - 123),
3. new type of biobriquettes with semi-cellulose as binding material (samples series 201 - 212) and
4. special biobriquettes.

Pure coal pieces "Soko" and "Borovica" were also subject to combustion for the purpose of comparison.

Schematic view of fire place, where the combustion took place and of measuring equipment is given in Fig. 5.9.

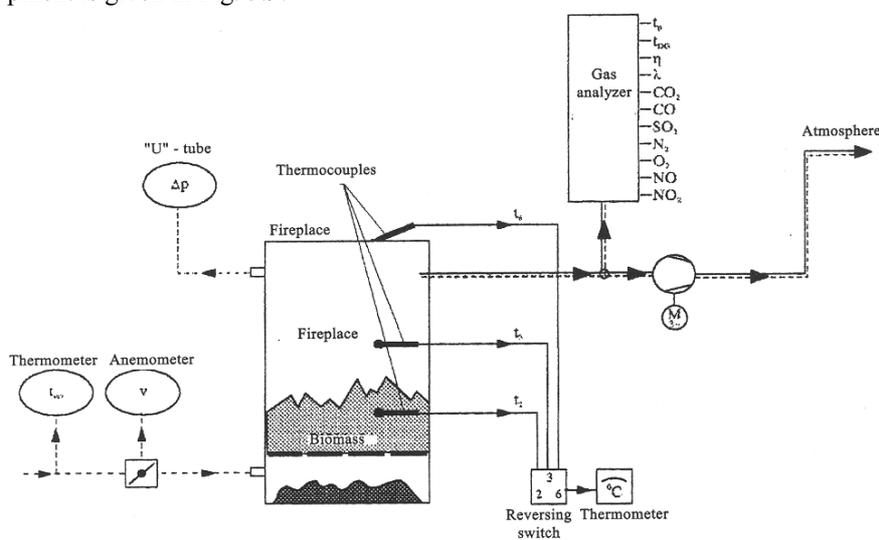


Fig. 5.9. Scheme of laboratory fire place and measuring spots for biobriquette combustion [5]

The frame of furnace for individual heating "Plamen1", domestic product, was used as experimental fire-place. It was adapted in the way that the following attachments for measuring equipment were fitted:

- two attachments for thermo-couple on the fire-place right side, of the diameter 34.5/28 mm, 10 cm from the grate for temperature measurement in the briquette layer and 27.5 cm from the grate for temperature measurement in the volatiles combustion zone;
- one attachment for sub-pressure measurement in the fire-place upper zone, i.e. in the volatiles combustion zone;

– one attachment for primary air introducing, tubes $\varnothing 42.4 \times 2.6 \times 1000$ mm with flow regulator. Thermometer is fitted on the tube for measuring inlet primary air temperature, as well as digital anemometer for primary air flow measurement.

Fire-place space dimensions are $175 \times 250 \times 445$ mm. Insulation was made by inserting refractory 40 mm thick brick, product of "Šamot - Arandjelovac" into the existing casing (Fig. 5.9.). The fire-place lower part is marked with cast structure of grate, ash container and rough armature of ash container door as well as the fire-place revision door. Primary and secondary air regulators have been fitted in the door, but were not used in this case, these were sealed instead. Fire-place upper part is built as adapted welded structure, incorporating: firing door (burner) and flue gases attachment (connection) $\varnothing 120$ mm. Temperature of casing was measured by contact thermometer at four spots, starting from the grate and each 100 mm upwards.

The experimental fire-place is connected to the fan by means of flue gas canal. Diameter of the flue gas canal in front of the fan is $\varnothing 120$ mm. The fan is connected to the hood for flue gases discharging via flue gases canal of rectangular section 180×118 mm.

During the experiment the following parameters have been measured:

Table 5.10. Review of parameters during the experiment [5]

No.	Parameter/measurement	Dimension	Equipment
1	Air velocity	[m/s]	Dough 435, measurement range 0,2 - 40 m/s
2	Inlet primary air temperature	[$^{\circ}$ C]	Thermocouple, type K, NiCr7023 IEC 584-1, Mi 7023, probe is AT0702 type - ISKRA Kranj, measurement range - 50 to 800 $^{\circ}$ C
3	Flue gases pressure in the space above the fire-place	[mmVS]	"U" tube
4	Temperature in the fire-place	[$^{\circ}$ C]	Thermocouple, type "S", class 2 56096/93, PtRh-Pt with compensation cable PtRh-Pr10%, measurement range 0 - 1500 $^{\circ}$ C
5	Temperature in volatiles combustion zone	[$^{\circ}$ C]	Thermocouple, type "K", NiCr-Ni, 109/84357/6 with compensation cable NiCr-Ni, measurement range 0 - 1200 $^{\circ}$ C
6	Temperature on the fire-place housing	[$^{\circ}$ C]	Thermocouple, type "K", NiCr-Ni, with compensation cable NiCr-Ni, measurement range 0 - 1200 $^{\circ}$ C
7	Temperature reading in the fire-place, volatiles and on the fire-place housing	[$^{\circ}$ C]	Thermocouple, type Ch5610 Wohlen, measurement range 0 to 1200 $^{\circ}$ C connected to compensation cables via reversing switch
8	Contents: O ₂ ; CO ₂ ; CO; NO; NO ₂ ; SO ₂ ; t _p ; t _{DG} ; λ η	[%] [mg/m ³] [$^{\circ}$ C] – [%]	Gas analyzer, type GAZOTEST TU4215-001-17763771-95, Russia, produced in September 1996., Gas analyzer, type Digitron Green Line, Germany, produced in January 1998. Gas analyzer Dough 300 XL-1
9	Briquette quantity	[kg]	House scale, laboratory balance
10	Briquette material quantity	[kg]	House scale, laboratory balance
11	Coal-dust quantity	[kg]	Laboratory balance
12	Lime-dust quantity	[kg]	Laboratory balance

Gas analyzer

Gas analyzer is attached to the flue gas canal. Dough 300 XL-1 was used to monitor flue gas analyses.

By means of gas analyzer Dough 300 XL-1 parameters shown in Table 5.11 may be measured.

Table 5.11. Review of parameters measured by gas analyzers Dough 300 XL-1

No.	Description	Mark	Unit	Measurement range	Accuracy
1.	Oxygen	O ₂	(%)	0-25	0.1 %
2.	Carbon dioxide	CO ₂	(%)	unlimited	0.1 %
3.	Carbon monoxide	CO	[ppm]	0-10 000	1 ppm
4.	Nitrogen monoxide	NO	[ppm]	0-3 000	1 ppm
5.	Sulfur dioxide	SO ₂	[ppm]	0 - 5 000	1 ppm
6.	Temperature	t	[°C]	-40 - +1 200	0.1 °C
7.	Differential pressure	Δp	[hPa] or [mbar]*	-80 - +80	0.01 hPa
8.	Dew point temperature	T _R	[°C]	0 - 99.9	0.1 °C
9.	Excess air	λ	[-]	0 – 20	0.01
10.	Combustion products speed	V	[m/cec]	–	0,1 m/cec
11.	Combustion products flow	Q	[kg/h]	–	1 kg/h
12.	Utilization coefficient gross/net	η	[%]	0 - 100	0,1

6. RESULTS TESTING

6.1. Sulfur sorbent effect to briquettes cubic mass

Sulfur sorbent effect to briquettes cubic mass was studied by comparing cubic masses of briquettes, that is, pallets of:

- wheat straw, without and with sulfur sorbent obtained by dry briquetting process [6,8] and
- coal-dust without and with sulfur sorbent, obtained by wet briquetting process with paper pulp, as binding agent (Table 6.1) [8].

Fig. 6.1. shows that the presence of sorbent effects the briquettes cubic mass; by increasing the sorbent share, the briquettes cubic mass is increased. That effect is more evident in briquettes obtained by dry procedure than in those obtained by wet procedure. In briquettes obtained by wet procedure there is the greater influence of CaCO₃ than Ca(OH)₂, onto the cubic mass, which can be understood, having in mind that the cubic mass of CaCO₃ = 1800 - 2800 kg/m³, and Ca(OH)₂ = 600 - 900 kg/m³.

Table 6.1. Effect of sulfur sorbent presence to briquettes cubic mass [6,8]

No.	Combustible material	Sorbent	Technological briquetting procedure	Binding agent	Share [kg/kg _b]	Cubic mass ρ [kg/m ³]
1.	Wheat straw	-	dry	-	1	1015
2.	Wheat straw	Ca(OH) ₂	dry	-	1	1060
3.	Coal-dust "Soko" - Citluk	-	wet	paper pulp	0,5/0,5	317
4.	Coal-dust "Soko" - Citluk	CaCO ₃	wet	paper pulp	0,477/0,5/0,023	312
5.	Coal-dust "Soko" - Citluk	CaCO ₃	wet	paper pulp	0,456/0,5/0,044	418
6.	Coal-dust "Soko" - Citluk	CaCO ₃	wet	paper pulp	0,437/0,5/0,063	388
7.	Coal-dust "Soko" - Citluk	CaCO ₃	wet	paper pulp	0,419/0,5/0,081	435
8.	Coal-dust "Soko" - Citluk	Ca(OH) ₂	wet	paper pulp	0,477/0,5/0,023	510
9.	Coal-dust "Soko" - Citluk	Ca(OH) ₂	wet	paper pulp	0,456/0,5/0,044	537
10.	Coal-dust "Soko" - Citluk	Ca(OH) ₂	wet	paper pulp	0,437/0,5/0,063	466
11.	Coal-dust "Soko" - Citluk	Ca(OH) ₂	wet	paper pulp	0,419/0,5/0,081	477

* In experiments indicated forming pressure in dry briquetting procedures was 300 bar, and in wet ones from 0,5 to 5 bar-a.

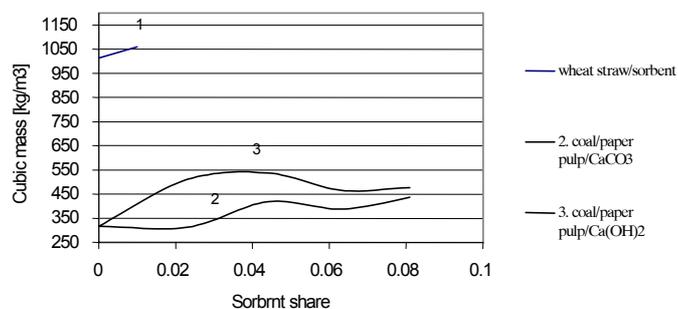


Fig. 6.1. Sulfur sorbent effect to briquettes cubic mass [4]

6.2. Sulfur sorbent effect to briquettes mechanical properties

Sulfur sorbent effect to briquettes mechanical properties was studied in the Faculty of Occupational Safety Combustion laboratory in 1997 and again in 1999, on coal and biomass briquettes, the technology of fabrication of which had been developed in the same laboratory.

Missing the adequate standards for biobriquettes testing, the following standards were used:

- JUS B. H8. 376 / 82 (Solid mineral fuels – Coal derived briquettes – Defining strength according to pressure) [1] and
- JUS G. S2. 813 / 90 (Hard plastic materials with cells – Test by pressing) [2].
- JUS B. H8. 376 / 82 Definitions of briquettes strength according to pressure - as pressure obtained with briquettes crushing.

The purpose of testing was to compare the resistance to pressure and the extent of relative deformation among various types of biobriquettes, i.e. biobriquettes of various cubic masses.

Having in mind that most biobriquettes are quite plastic and that great relative deformations are achieved without the briquettes destruction, the authors (following JUS G. S2. 813 / 90), define pressure strain (stress) σ_{10} as a quotient of pressure force at 10 % of relative deformation ϵ_{10} and the sample cross-section surface. At that, relative deformation ϵ understands the quotient of sample height reduction compared to its initial value and it is calculated in percentage.

Test method is described in detail in references 1 and 4.

The first test is related to composite briquettes of dark lignite coal "Soko", calcium-carbonate of lime and non-metal industry "Ostrovica" and hydrated lime of trade origin for commercial needs.

When producing composite biobriquettes based on ligno-cellulose pulp, coaldust, calcium-carbonate and hydrated lime, molar ratios of calcium to sulfur Ca / S were established and they are 1; 2; 3; 4 as well as for composite briquettes comprising paper-coaldust, without addition of the third component. Test material is described in detail in [1].

Test procedure according to JUS B. H8. 376 foresees placing of test briquette between the cylindrical press attachments so that the attachments act on the briquette central surface. Then the press is switched on, the pressure is being evenly increased to the point of briquette crushing, and the maximum pressure is recorded.

The test results, as protocol extracts, are shown in Table 6.2. and in Fig. 6.3. The most important statement is that within the pressure range from 1 to 4 MP, there were no briquettes crushing. Briquettes underwent some permanent plastic deformations, in the way that cylinder height was decreased and cylindrical shape turned into barrel shape. The samples kept elastic properties so that after their removing from the press, their height somewhat increased. During the pressure acting on briquettes, there was breaking or crushing of incorporated rigid biomaterial particles within briquettes, but not briquettes breaking.

The smallest deformations (in view of briquettes getting the barrel shape) were obtained on light composite briquette of coaldust and sulfur sorbent.

Table 6.2. Test results of light composite biobriquettes in view of their pressure resistance [3]

No.	Briquettes composition	Pressure (MPa)	ϵ (%)	Comment
1	Coaldust /paper/ CaCO ₃	3	55	Cylindrical shape was preserved, straight cylinder partially turned into oblique, no cracks or crushing observed
2	Coaldust /paper/ (CaOH) ₂	3,93	35	Cylindrical shape was preserved, straight cylinder partially turned into oblique, no cracks or crushing observed

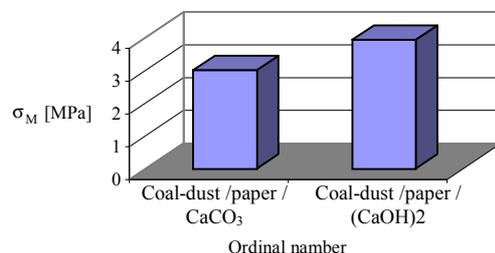


Fig. 6.2. Sulfur sorbent effect to pressure resistance of composite briquettes made of coaldust "Soko" and sulfur sorbent, obtained by wet briquetting procedure [3]

Subsequent test was carried out on more than 40 samples of various biobriquettes types. There are 14 samples presented, classified in 5 different series: 1. 2. 3. 4. and 5 (Table 6.3.). Classification into these groups was done according to briquettes composition. Briquettes of 1. 2. and 3. groups were obtained by wet procedures and those of 4. and 5. group – were obtained by dry procedure.

The combustible components used were wheat straw and coaldust and binding agents for briquettes obtained by wet procedure were semi-cellulose and paper pulp. Semi-cellulose represents a binding agent of a new biobriquette type, produced in the Faculty of Occupational Safety Combustion laboratory. It is derived from straw, by a corresponding procedure and it could also be obtained from other non attractive plants parts.

In producing composite biobriquettes based on coaldust "Soko" (granulate 0–15 mm), the sorbents used were hydrated lime (powder) and limestone "Ostrovica" (granulate 0–2,5 mm), with molar ratio established of $\text{Ca/S} = 1, 2, 3$ and 4. These tests refer to briquettes with hydrated lime incorporated as sorbent.

Basic composition and certain component shares are presented in Table 6.3.

Other procedure according to JUS G. S2. 813 / 90 was applied because of similarity in biobriquettes structure obtained by wet procedure, to structure of plastic materials with cells. According to this procedure the following is determined:

- pressure resistance and relative deformation or
- pressure strain at 10 % of relative deformation.

The procedure is based on sample placing between two plates of the compression test machine. During the test the plates move at constant speed. Depending on the test requirements the force and length of test bar is measured and pressure, that is, strain and relative deformation are calculated.

This procedure was carried out in the Faculty of Occupational Safety Combustion laboratory Fig. 5.8.

Briquette was placed between two plates, and then the pressure was gradually increased. During the test, the hydraulic system pressure and briquette length were measured; the average initial length of biobriquette was around 100 mm. Relative deformation ϵ_{10} was calculated on the basis of briquette sample reduction and its initial length. Pressure strain σ_{10} was obtained by recalculation of the read pressure in the press hydraulic cylinder against the pressure attained on the briquette surface (according to JUS G. S2. 813 / 90), at that, 10% of relative deformation was attained.

The test results are shown in Table 6.3. and Figures 6.3. and 6.4.

Table 6.3. Biobriquette types and test results at relative deformation $\epsilon_{10}= 10\%$ [3]

Series No.	Obtain procedure	Briquette No.	Briquette composition	Share	Cubic mass [kg/m ³]	Ca/S	σ_{10} [MPa]	σ_M [MPa]
1.	Wet	1.1.	Semi-cellulose Coal dust	0,1 0,9	864	–	0,432	0,61
		1.2.	Semi-cellulose Coal dust	0,20 0,80	783	–	0,549	
		1.3.	Semi-cellulose Coal dust	0,30 0,70	724	–	0,432	
2.	Wet	2.1.	Paper pulp Coal dust	0,1 0,9	738	–	0,555	1,43
		2.2.	Paper pulp Coal dust	0,2 0,8	588	–	0,667	
		2.3.	Paper pulp Coal dust	0,3 0,7	558	–	0,667	
		2.4.	Paper pulp Coal dust	0,4 0,6	548	–	0,679	
		2.5.	Paper pulp Coal dust	0,5 0,5	440	–	0,726	
3.	Wet	3.1.	Paper pulp Coal dust Hydrated lime	0,1 0,86 0,04	817	1	1,137	2,006
		3.2.	Paper pulp Coal dust Hydrated lime	0,1 0,82 0,08	833	2	1,255	
		3.3.	Paper pulp Coal dust Hydrated lime	0,1 0,79 0,11	818	3	1,255	
		3.4.	Paper pulp Coal dust Hydrated lime	0,1 0,75 0,145	730	4	1,137	
4.	Dry	4.	Wheat straw Hydrated lime	0,97 0,03	1060	8,36	–	27,16
5.	Dry	5.	Wheat straw	1	1015	–	–	19,21

Based on the above shown various biobriquettes pressure resistance test results obtained at the Faculty of Occupational Safety Combustion Laboratory, it can be concluded that:

1. Admixtures, although having a very small share, significantly effect biobriquettes mechanical properties;

2. Briquettes with semi-cellulose as binding material have satisfactory mechanical properties, related to manipulative storage operations. On the other hand, they are more subject to destruction than briquettes with paper pulp as binding material;

3. Briquettes obtained by dry procedure may endure higher pressures and deformations than briquettes obtained by wet procedure, and not to be destroyed. However, at pressure force transversal action, these briquettes crack, effected by far less pressure forces. It has also been observed that longer than 2 months period of storage in normal conditions causes briquettes cracking both in longitudinal and transversal directions due to weakening of inter-elastic binding forces. In case of briquettes obtained by wet procedure there is no such a phenomena [3].

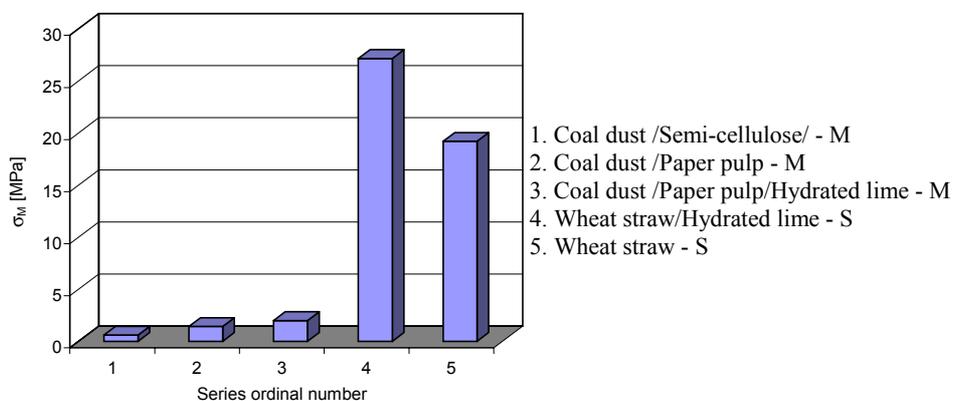


Fig. 6.3. Sulfur sorbent and kinds of briquetting technological procedures effects (M - wet; S - dry) on composite briquette pressure resistance [3]

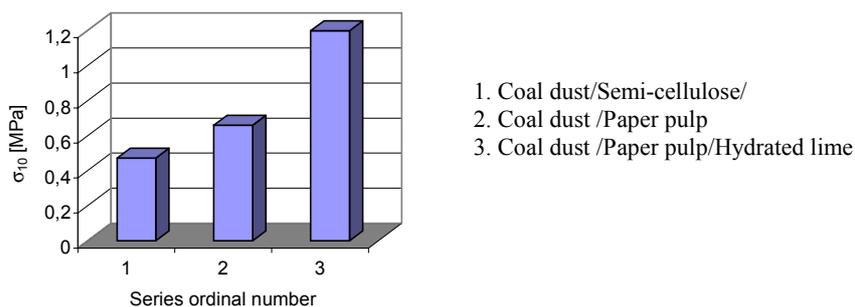


Fig. 6.4. Pressure strain dependence on briquette type and sulfur sorbent presence at 10 % of relative deformation [3]

6.3. Sulfurization degree test results

Sulfurization degree was tested on 5 series of composite briquettes, (Table 6.4.):

- A – coal dust "Soko" / paper pulp
- B - coal dust "Soko" / paper pulp / lime-stone "Ostrvica",
- C - coal dust "Soko"/ paper pulp / hydrated lime,
- D - beech/coal "Borovica" and
- E - beech/coal "Borovica"/lime-stone "Visocica".

Table 6.4. Composite briquettes series, combustion and desulfurization degree parameters [4]

Series	Test Ord.No.	Briquet. Ord. No.	Share	(Ca/S) ^M	λ [-]	t [°C]	$u_{SO_2}^{ul} \left[\frac{m^3_{SO_2}}{m^3_{PSs}} \right]$	$u_{SO_2}^{iz} \left[\frac{m^3_{SO_2}}{m^3_{PSs}} \right]$	η [-]	
A - coal dust "Soko" / paper pulp	9	102	0.95/0.05	0	1.7	785	0.122722	0.043877	0.642464	
	10			0	2.16	765	0.096285	0.032716	0.660222	
	11			0	2.19	720	0.094952	0.042128	0.556321	
	12			0	1.68	700	0.124204	0.037859	0.695187	
	13	103	0.9/0.1	0	1.65	820	0.207479	0.073829	0.644162	
	14			0	2.41	805	0.141333	0.047167	0.666275	
	15			0	3	780	0.113294	0.03499	0.691157	
	16			0	1.89	765	0.180763	0.050211	0.72223	
	17	104	0.8/0.2	0	2.18	890	0.082514	0.046117	0.441102	
	18			0	2.2	870	0.081753	0.044752	0.452596	
	19			0	2.61	840	0.068764	0.042758	0.378191	
	20			0	1.44	815	0.125807	0.060218	0.521349	
	21	105	0.7/0.3	0	2.7	840	0.060188	0.024178	0.598291	
	22			0	3.29	805	0.049286	0.038524	0.218352	
	23			0	4.82	780	0.033534	0.027642	0.175688	
	24			0	3.01	690	0.053921	0.032191	0.403	
	25	106	0.6/0.4	0	7.76	750	0.018662	0.012037	0.355018	
	26			0	5.8	700	0.025008	0.011967	0.521485	
	27			0	4.22	650	0.034452	0.014346	0.583592	
	28			0	4.17	610	0.034868	0.021764	0.375828	
	29	107	0.5/0.5	0	4.21	700	0.030351	0.010112	0.666826	
	30			0	4.49	710	0.028441	0.015746	0.446389	
	31			0	7.22	650	0.017629	0.011057	0.372788	
	32			0	3.75	580	0.034113	0.01858	0.455351	
	B - coal dust "Soko" / paper pulp / lime "Ostrvica"	33	108	0.86/0.1/0.04	1	3.98	640	0.049254	0.020609	0.581579
		34			1	3.44	685	0.057046	0.025648	0.550405
		35			1	3.84	665	0.051063	0.023548	0.538836
		36			1	2.47	620	0.079691	0.030756	0.614058
		37	109	0.82/0.1/0.08	2	4.47	740	0.043792	0.012981	0.703567
		38			2	3.63	710	0.054	0.019279	0.642973
		39			2	5.57	680	0.035102	0.014451	0.588317
		40			2	3.07	600	0.063936	0.022988	0.640448
41		110	0.79/0.1/0.11	3	7.25	630	0.026674	0.015431	0.421505	
42				3	3.6	620	0.05392	0.031526	0.415319	
43				3	5.8	600	0.033373	0.019839	0.405526	
44				3	2.95	590	0.065909	0.03485	0.471242	
45		111	0.755/0.1/0.145	4	3.04	775	0.063893	0.038139	0.403079	
46				4	3.18	760	0.061056	0.03422	0.439529	
47				4	3.23	740	0.060103	0.03331	0.445778	
48				4	2.59	670	0.075111	0.029672	0.604962	
49		112	0.477/0.5/0.023	1	2.57	825	0.049262	0.022604	0.541155	
50				1	3.23	800	0.039071	0.015571	0.601482	
51				1	6.15	710	0.0204	0.010322	0.494021	
52				1	3.26	600	0.038707	0.013996	0.638413	
53		113	0.456/0.5/0.044	2	3.94	750	0.031471	0.010637	0.66201	
54				2	5.14	740	0.024066	0.008748	0.636526	
55				2	6.3	680	0.019607	0.008293	0.577054	
56				2	2.86	640	0.043524	0.013226	0.696114	
57		114	0.437/0.5/0.063	3	5.94	740	0.020484	0.007278	0.64471	
58				3	5.85	700	0.020802	0.009832	0.527339	
59				3	6.91	660	0.017592	0.008922	0.492815	
60				3	2.9	620	0.04226	0.012771	0.69779	
61		115	0.419/0.5/0.081	4	5.94	760	0.020166	0.012631	0.373631	
62				4	3.77	730	0.0319	0.014801	0.536023	
63				4	4.75	720	0.025262	0.012701	0.497208	
64				4	2.65	670	0.045591	0.015536	0.659244	

Series	Test Ord.No.	Briquet. Ord. No.	Share	(Ca/S) ^M	λ [-]	t [°C]	$u_{SO_2}^{ul} \left[\frac{m^3_{SO_2}}{m^3_{PSs}} \right]$	$u_{SO_2}^{iz} \left[\frac{m^3_{SO_2}}{m^3_{PSs}} \right]$	$\eta [-]$
C - coal dust "Soko" / paper pulp / hidrated lime	65	116	0.876/0.1/0.024	1	3.1	780	0.073022	0.03569	0.511248
	66			1	3.28	750	0.069326	0.036145	0.47863
	67			1	3.65	740	0.062793	0.030336	0.516887
	68			1	2.29	700	0.096069	0.032121	0.665649
	69	117	0.854/0.1/0.046	2	3.48	740	0.06562	0.018755	0.714192
	70			2	3.07	730	0.073659	0.021169	0.71261
	71			2	4.37	710	0.053051	0.01739	0.672199
	72			2	2.69	640	0.083095	0.020189	0.757035
	73	118	0.832/0.1/0.068	3	3.26	800	0.069673	0.027327	0.607778
	74			3	4.2	780	0.055042	0.0183	0.667533
	75			3	5.58	720	0.042072	0.012596	0.700601
	76			3	3.5	620	0.065245	0.009797	0.84984
	77	119	0.812/0.1/0.089	4	3.96	760	0.058135	0.018265	0.685822
	78			4	5.23	730	0.044727	0.012491	0.720719
	79			4	3.98	680	0.057862	0.040658	0.297322
	80			4	2.46	650	0.090002	0.016375	0.818056
	81	120	0.487/0.5/0.013	1	4.35	730	0.034562	0.012561	0.636552
	82			1	3.49	705	0.042443	0.019524	0.539982
	83			1	6.64	660	0.023127	0.006473	0.720104
	84			1	2.75	620	0.052803	0.011862	0.775361
	85	121	0.474/0.5/0.026	2	3.06	740	0.047213	0.020399	0.567933
	86			2	3.45	730	0.042279	0.019734	0.533232
	87			2	4.84	720	0.030804	0.011337	0.631975
	88			2	2.16	695	0.064616	0.023583	0.635024
	89	122	0.462/0.5/0.038	3	3.88	790	0.038884	0.018125	0.533876
	90			3	3.3	780	0.045181	0.024353	0.460984
91	3			3.61	750	0.041582	0.023618	0.432004	
92	3			2.24	680	0.064171	0.014416	0.775354	
93	123	0.451/0.5/0.049	4	3.99	780	0.036358	0.014661	0.596767	
94			4	7.83	510	0.019147	0.004724	0.753294	
95			4	3.07	505	0.046338	0.002589	0.944122	
96			4	3.17	500	0.044995	0.004584	0.898129	
D - beech/coal "Boroviča"	176	308	0.7/0.3	0	2.5	560	0.021251	0.001295	0.93908
	177			0	2.4	600	0.022042	0.001505	0.93174
	178			0	1.3	590	0.037311	0.00021	0.994373
E - beech/coalj "Boroviča"/lime "Visočica"	163	304	0.7/0.29/0.01	1	4.39	620	0.010771	0.000175	0.983758
	164			1	5.55	630	0.008501	0.000315	0.962956
	165			1	6.3	625	0.007482	0.00049	0.934524
	166			1	2.81	440	0.016929	0.002344	0.861517
	167	305	0.7/0.283/0.007	2	2.4	960	0.01919	0.003709	0.806728
	168			2	1.6	965	0.02907	0.003709	0.872415
	169			2	2.7	930	0.017021	0.003289	0.806763
	170	306	0.7/0.279/0.025	3	2.2	790	0.020969	0.003709	0.823121
	171			3	2.3	785	0.020038	0.003289	0.835863
	172			3	4.5	640	0.01014	0.000315	0.968945
	173	307	0.7/0.268/0.032	4	1.8	750	0.02483	0.004689	0.811167
174	4			1.8	750	0.02483	0.004514	0.818213	
175	4			4	720	0.011014	0.001015	0.907868	

Absolute and relative desulfurization degrees for each briquette series, at similar combustion parameters are shown in subsequent Tables and Figures (Tables 6.5, 6.6, 6.7, 6.8. and 6.9; Figures 6.5, 6.6, 6.7, 6.8. and 6.9)

Table 6.5. Absolute and relative desulfurization degrees for composite briquette made of coal dust "Soko", paper pulp and CaCO_3 , with coal-dust share of 0.8 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Series	Briquette Ord. No.	$(\text{Ca/S})^M$	η_A	η_R
A	104	0	0.521	–
B	108	1	0.550	0.029
	109	2	0.703	0.153
	110	3	0.421	-0.282
	111	4	0.403	-0.018

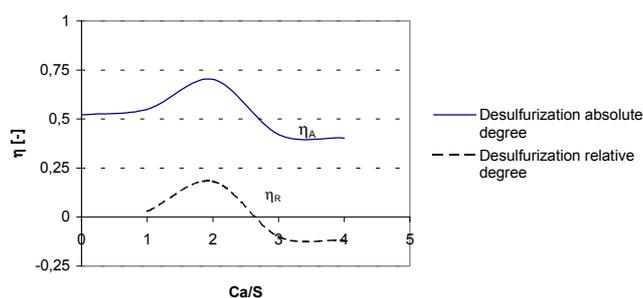


Fig. 6.5. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and CaCO_3 , with coal-dust share of 0.8 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Table 6.6. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and CaCO_3 , with coal-dust share of 0.5 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Series	Briquettes Ord. no.	$(\text{Ca/S})^M$	η_A	η_R
A	107	0	0.446	-
B	112	1	0.49	0.044
	113	2	0.636	0.146
	114	3	0.6447	0.0087
	115	4	0.536	-0.1087

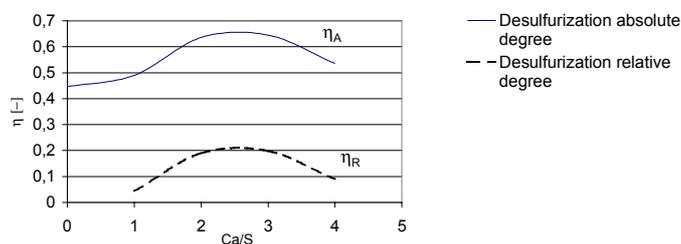


Fig 6.6. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and CaCO_3 , with coal-dust share of 0.5 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Tabela 6.7. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and $\text{Ca}(\text{OH})_2$, with coal-dust share of 0.8 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Series	Briquette Ord. No.	$(\text{Ca}/\text{S})^{\text{M}}$	η_{A}	η_{R}
A	104	0	0.521	
C	116	1	0.511	-0.01
	117	2	0.714	0.193
	118	3	0.700	0.179
	119	4	0.720	0.199

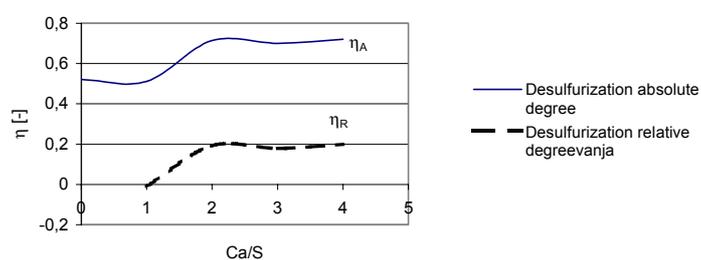


Fig 6.7. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and $\text{Ca}(\text{OH})_2$, with coal-dust share of 0.8 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Tabela 6.8. Absolute and relative desulfurization degrees for composite briquettes of coal-dust "Soko", paper pulp and $\text{Ca}(\text{OH})_2$, with coal-dust share of 0.5 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Series	Briquette Ord. No.	Ca/S	η_{A}	η_{R}
A	107	0	0.446	
C	120	1	0.636	0.19
	121	2	0.635	0.189
	122	3	0.775	0.329
	123	4	0.596	0.15

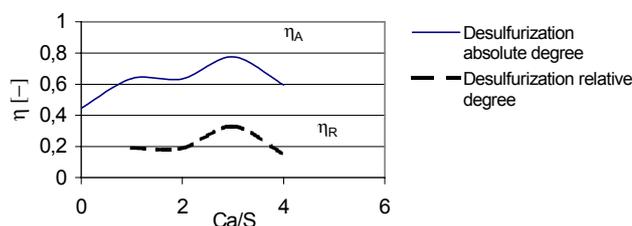
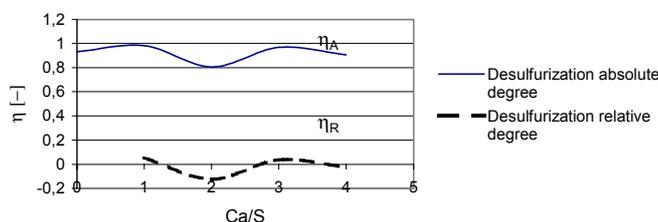


Fig 6.8. Absolute and relative desulfurization degrees for composite briquettes made of coal-dust "Soko", paper pulp and $\text{Ca}(\text{OH})_2$, with coal-dust share of 0.5 and combustion temperature of around $700\text{ }^\circ\text{C}$ [4]

Table 6.9. Absolute and relative desulfurization degrees for composite briquettes made of brench sawdust, coal-dust "Borovica", and CaCO_3 , with coal-dust share of 0.8 and combustion temperature of around 700 0C [4]

Series	Briquette Ord. No.	Ca/S	η_A	η_R
D	177	0	0.93174	–
E	304	1	0.983	0.052
	305	2	0.806	-0.125
	306	3	0.968	0.037
	307	4	0.907	-0.024

* In case of combustion of coal "Borovica" pieces at temperature of 730 0C, self-desulfurization degree us 0,98.



Fif 6.9. Absolute and relative desulfurization degrees for composite briquettes made of brench sawdust, coal-dust "Borovica", and CaCO_3 , with coal-dust share of 0.8 and combustion temperature of around 700 0C [4]

7. CONCLUSIONS

The presence of sorbent in composite briquettes slightly increases the briquette **cubic mass** with the increase of sorbent share. After the sorbent share of 2 – 3% was attained, significant increase of the cubic mass stops.

Mechanical properties of briquettes obtained by wet procedure are significantly different from the properties of briquettes obtained by dry procedure. The former are incomparably more stable when stored, do not crack, their inter-elastic forces are not weakened, and when exposed to pressure they are not destructed, but only undergo significant plastic deformations. Unlike these, briquettes obtained by dry procedure are destructed after attaining the pressure forces critical values. They crack in transversal direction under the action of far less pressure forces vales.

In **desulfurization** processes:

- molar ratio Ca/S in briquettes obtained by wet procedure with CaCO_3 as a sorbent, has the optimum value $(\text{Ca/S})^M \approx 2$, when $\eta_A = 0,7$ (absolute desulfurization degree) and $\eta_R = 0,2$ (relative desulfurization degree) are attained for dark lignite coal "SOKO". At that, the ratio fuel/ binding matter/ sorbent, ranges as follows: 0,86/0,1/0,04; 0,82/0,1/0,008; 0,79/0,1/0,11 and 0,755/0,1/0,145.
- The increase of binding matter share in such briquettes shifts the optimum value of molar ratio Ca/S to higher values. In that way, maximum value of desulfurization

degree is attained for $(Ca/S)^M = 2,5$ when the ratio of fuel and binding material is established at values 0,477/0,5/0,023; 0,456/0,5/0,044; 0,437/0,5/0,063;

- Any further increase of molar ratio Ca/S has no sense, because the desulfurization degree, having attained the maximum value, reduces desulfurization effect.
- The common conclusion, regarding experiments with $CaCO_3$ as a sorbent, is that after the maximum values of desulfurization effects have been attained, this effect is being minimized by further sorbent addition. It is most probable that the sorbent effective surfaces are decreased, due to great molar volume of sulfate, and in that way the surfaces of non-reacted CaO are blocked. Such a conclusion is intuitive and must be the subject of further research.
- Further increase of molar ratio Ca/S from the value $(Ca/S)^M$ at which η_{ma3} is attained, is not that significant when the sorbent used is $Ca(OH)_2$. In that case, there is a slight decrease of desulfurization degree and it can be regarded that after attaining the maximum value, desulfurization degree is almost a constant.
- In briquettes obtained by wet procedure from the coal "SOKO", maximum value of absolute desulfurization degree is $\eta_A = 0,7$ and of relative desulfurization degree $\eta_R = 0,2$ at molar ratio $(Ca/S)^M \approx 2$ for $Ca(OH)_2$ sorbent.
- In briquettes with reduced share of combustible material (coal "SOKO") the increase of binding matter share in such briquettes is manifested in the same way as in case of $CaCO_3$ as a sorbent.
- In composite briquettes made of "Borovica" coal, a high degree of self-desulfurization was found, which is most probably the effect of mineral admixtures composition within this type of coal. It was shown that in briquettes bio-coal, composed of "Borovica" coal, practically it was not necessary to add sorbent and in such case, it had no effect.

It can be concluded that in production of composite briquettes, by wet and dry procedures, flue gases desulfurization degrees may be attained in the order of 70 ÷ 90% by sulfur sorbent addition. Optimum value $(Ca/S)^M$ must be established experimentally for each type of coal and sorbent, due to significant share of self-desulfurization, characteristic for each coal type in a particular way.

REFERENCES

1. JUS B. H8. 376 / 82. god – Solid mineral fuels – Coal briquettes – Defining resistance according to pressure
2. JUS G. S2. 813 / 90. god. – Hard plastic cellular materials - Compression test
3. Mihajlovic, Emina, Mitic, D., Nestic, B., Milanovic, B., Jankovic, Slobodanka.: Comparative characteristics of resistance according to pressure of various biobriquettes types, PTEP – Process technique and power engineering in agriculture journal, Novi Sad, 3,1999.
4. Mihajlović, Emina: Sulfur sorbent effect to desulfurization degree, Internal report of the Faculty of Occupational Safety Combustion and Thermal Technique Laboratory in Nis No. 299, 27. 09. 2002 - 23. 11. 2002.
5. Milanović B.: "Biobriquettes basic research and fire protection of their production and use plants ", Master thesis, Faculty of Occupational Safety in Niš, Niš, 2000.
6. Mitic, D., Mihajlovic Emina, Nestic, B.: Internal report of the Faculty of Occupational Safety Combustion and Thermal Technique Laboratory in Nis No. 88 -1998.

7. Mitić, D., Mihajlović Emina: Methods of combustion temperature calculation, Faculty of Occupational Safety (Fakultet zaštite na radu), Nis, 2000.
8. Mitić, D., Nesić, B., Janković, Slobodanka: Light composite briquettes physical characteristics, Facta universitatis, University of Nis, 1 (1997) 2, s. 51- 59.
9. Mitić, D.: Biomasses and briquettes of Serbia-potential ecological fuels, monograph, Jugoslovensko društvo za procesnu tehniku i energetiku u poljoprivredi-Novi Sad, Agricultural Faculty (Poljoprivredni fakultet), Novi Sad, Jugoslovenski savez inženjera i tehničara zaštite-Nis, Novi Sad, 1998.
10. Mitić, D.: Modeling of combustion and desulfurization process in fluidized bed for domestic coals PhD Thesis, Faculty of Mechanical Engineering, University of Niš, Niš, 1990.
11. Mitić, D.: Stechiometrical calculations in combustion processes, Jugoslovenski Savez inženjera i tehničara zaštite, "Monograf", Novi Sad, 2001.

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SORBENT SUMPORA U KOMPOZITNIM BRIKETIMA

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Osnovu kompozitnog briketa čine biomasa i sitne frakcije uglja (kao predstavnika fosilnog goriva), eventualno vezivi materijal i sorbent sumpora. U izvesnim slučajevima sorbent sumpora preuzima ulogu i vezivog materijala. Kao takav, kompozitni briket pruža izvesne mogućnosti iskorišćenja ugljeva sa značajnim sadržajem sumpora tako što će se iz dimnog trakta eliminisati SO₂. Proces odsumporavanja vrši se u samom ložištu vezivanjem nastalog sumpordioksida uz čvrste produkte sagorevanja u obliku sulfata. Autori su za svoja istraživanja koristili kompozitne brikete dobijene suvim i mokrim postupcima, a kao sorbente koristili su kalcijum karbonat i kreč. U slučajevima kada je korišćen kreč, on je imao i funkciju vezivnog materijala. Ispitivanja obuhvataju:

- teorijski pristup procesu odsumporavanja;
- prateće termičke efekte kod upotrebe sorbenta;
- detaljan opis primenjenih materijala i metode istraživanja;
- uticaj sorbenta na mehanička svojstva briketa;
- analizu efekata apsolutnog i relativnog stepena odsumporavanja i
- uticaj molarog odnosa Ca/S na stepen odsumporavanja.