

Metallurgical fuel production from low-metamorphism coals after their chemical treatment

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It is known, that strong lamp metallurgical coke is produced at laminar coking process of coal charges which are blended from baking coals of medium stages of metamorphism ($C^{daf} = 80-87\%$). These coals account a few percents only from total coal production, are critical and expensive. High price of baking coals determines prime cost of coke and limits its production increase.

More than 90% of coal world's supply fall at low-metamorphism coals (LMC) – lignite and candle coals. However, it is impossible to obtain strong lump metallurgical coke from such coals by means of traditional laminar coking process. The reasons of this are high yield of the volatile matter with small molecular weight and absence of liquid non-volatile substances (LNS) with medium molecular weight (200-300 c. u.). As a result, volatile matter leaves coal charge at the temperature much less ($350\text{ }^{\circ}\text{C}$) than temperature of coal char single structure ($450-500\text{ }^{\circ}\text{C}$). Plastic layer is not formed because of absence of liquid contact zone between coal grains and pyrolysis solid residue is disintegrated into powder.

In chemical-physical respect LMC are polymorphous tertiary structure (conglomerate), which is formed from molecular fragments with small molecular weight (primary structure) [1, 2]. Properties of tertiary structure are determined by non-valency linkages between polar functional groups – electron donors (aromatic, aliphatic, naphthenetic) groups and electron-seeking (carboxyl, carbonyl, hydroxyl and sulfide too) ones. At pyrolysis process of coal tertiary and secondary coal structure destruction starts with these linkages rupture at the temperature about $350\text{ }^{\circ}\text{C}$. This temperature, however, is higher than boiling-point of small molecular weight of by-products of LMC pyrolysis, which leaves coal charge quickly.

It was showed in works [3, 4], that during metamorphism of coals at the temperature $250-320\text{ }^{\circ}\text{C}$ chemical reactions of dehydration and decarboxylation and aromatic condensation reactions of coal organic structure natural conditions when volatile by-products do not leave coal. They generate multinuclear naphthenetic and aromatic structures with medium molecular weight which correspond to gas, fat and coke coals. In that way, target of strong lamp metallurgical coke production from LMC consists in change of chemical mechanism of coal pyrolysis in order to generate LNS in adequate amount for forming of plastic layer (30%).

Put problem has been solved by means of conditions for chemical reactions of LMC dehydration and decarboxylation and aromatic condensation reactions at comparatively low temperature and pressure in order to such conditions could be introduced into industry. So, inexpensive catalysts, solvents and reagent for such reactions in liquid phase were found. We used aliphatic hydrocarbons as solvents, polyenes and aromatic hydrocarbons as reagents.

Experimental technique:

High-boiling solvent (boiling-point 350°C), was prepared from large-tonnage industrial and domestic waste according special technology. Reagents, made of large-tonnage industrial waste too with special catalysts were added in amount 10, 20, 30, 40 and 50% to lignite after predrying (moisture 15%). Then we added 20% solvent to lignite-reagent mixture and kept it 24 hours at $250\text{-}350^{\circ}\text{C}$. Pyrolysis of lignite-reagent mixture was realized in stainless steel retort, heating rate was $1,5^{\circ}\text{C}/\text{min}$. up to 900°C . At this temperature charge was kept for 1 hour, cooled and elicited from retort. We caught and studied volatile matter according to standard method, made up a balance. Solvent was condensed together with coal-tar pitch and divided by means redistillation at 350°C . Fixed residue was studied according to standard method, which used for coke study in laboratory environment. Analogous experiments was conducted with candle coal.

Plastic properties of chemical treated coals determined by Institute of Fossil Fuel (Russian Science Academy).

RESULT:

Fixed residue yield is showed in fig.1. It is obviously that yield maximum corresponds to 30% reagents addition. At that fixed residue of the process without reagents and catalysts addition shaped fine-dyspersated. But fixed residue with 10% addition shaped small-sized, with 20-50 % addition - lumpy.

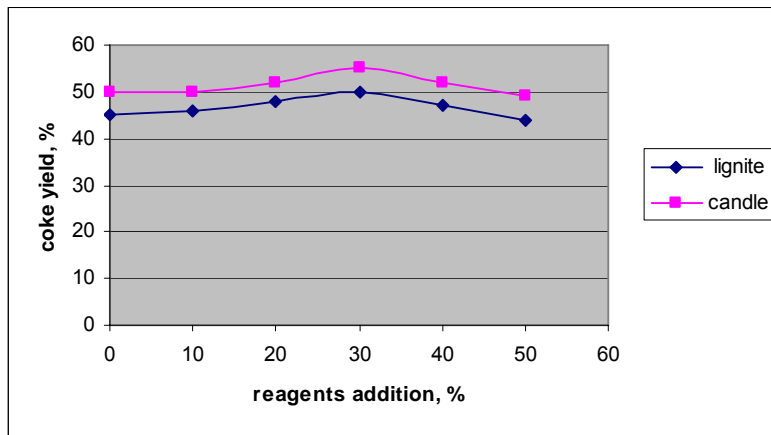


Fig. 1. Coke yield from coal-reagent mixtures.

Quality indexes of coke is showed in fig. 2 and 3.. Durability of coke increase naturally at reagents part increase up to 30%, then became stabilize.

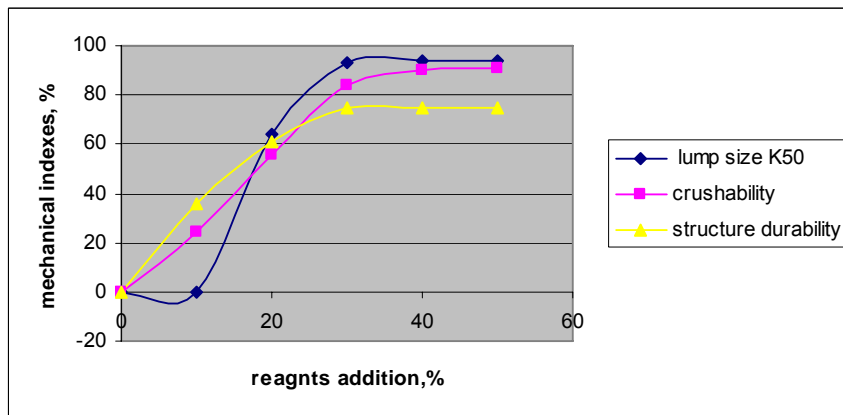


Fig. 2. Quality indexes of coke from lignite-reagent mixtures.

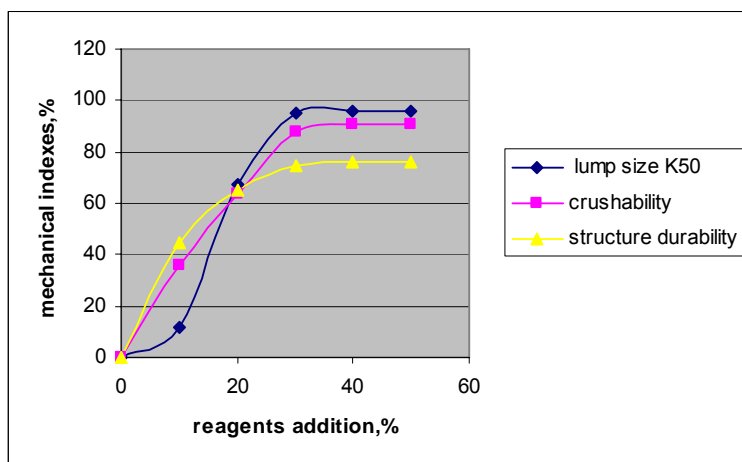


Fig. 3. Quality indexes of coke from candle coal-reagent mixtures.

Yield of liquid pyrolysis by-products (except for mass of overhead solvent) is showed in fig. 4. It was found that yield of liquid by-products rises sharply at addition more than 30% reagents. Qualitative analysis revealed presence of aromatic, aliphatic, naphthenetic hydrocarbons.

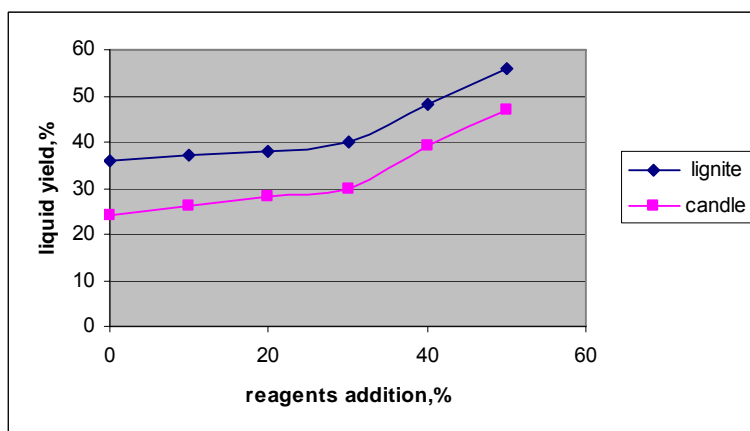


Fig. 4. Yield of liquid by-products from coal-reagent mixtures.

Change of plastic properties of treated lignite and candle coal are showed in fig. 5. and fig. 6. According to increase of reagents share up to 30% shrinkage x decreases but then increases. Plastic layer thickness y increases up to 14 mm in lignite and 19 in candle coal at 30% reagents and more.

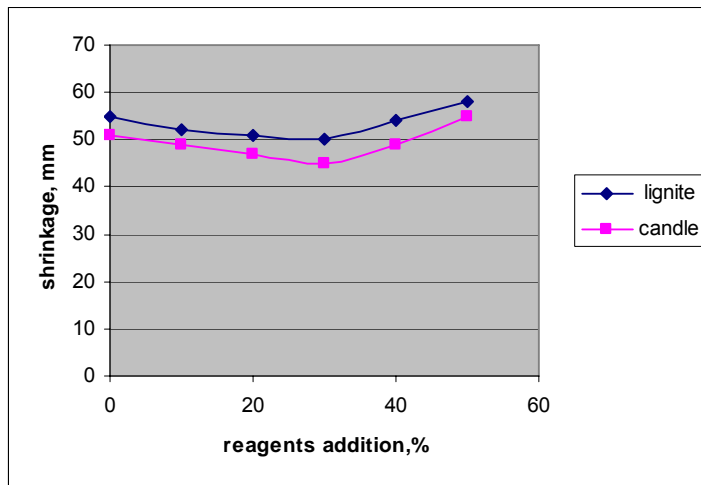


Fig. 5. Shrinkage of coal-reagent mixtures.

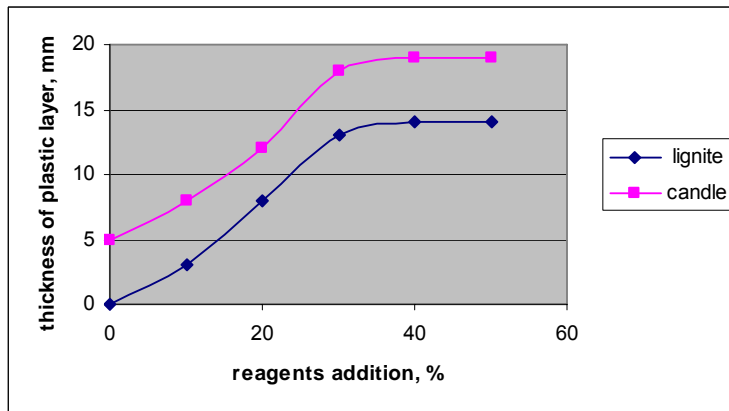


Fig. 6 Plastic layer thickness of coal-reagent mixtures.

DISCUSSION:

Formula, determined by approximation method, describes fixed residue yield from lignite- reagents mixture, has view:

$$M_c = 0,45M_l + 0,80M_r,$$

where M_c – fixed residue yield from mixture;
 M_l – lignite share;
 M_r – reagents share;
 0,45 – fixed residue yield from lignite;
 0,80 – reagents rate of use.

Formula, determined by approximation method, describes fixed residue yield from candle coal - reagents mixture, has view:

$$M_c = 0,50M_{cl} + 0,80M_r$$

where M_c – fixed residue yield from mixture;
 M_{cl} – candle coal share;
 M_r – reagents share;
0,50 – fixed residue yield from candle coal;
0,80 – reagents rate of use.

Reagents rate of use depends on chemical reactions type - in this case additive reactions – and is approximately equal carbon content in it. It means that 80% mass of reagents turns into coke and 20% - in volatile matter. As it follows from formulas, that at constant reagents rate of use 0,80 maximal reagents consumption is 30% from mixture mass. Reagents surplus is not consumed for coke formation but it is decomposed and goes out together with volatile matter. This is a reason of liquid by-products yield increase. Therefore, reagents rate of use for coke formation is conditioned by chemical reaction ability of coal and depends on content of definite functional groups on coal organic mass.

Increase of lump coke strength at reagents addition is evidence of coal pyrolysis chemical mechanism change, generation of LNS and increase of plastic properties. Increase of plastic layer thickness y increases up to 14 mm in lignite and 19 in candle coal e.i. up to fat and coke level is a such evidence too. Probably, these changes are result of decrease of decomposition reactions temperature, and consequently widening of temperature interval of coal plastic state. Strength of lump coke made of such coal allows use it as blast-furnace fuel.

Low coke yield from LMC comparatively to coal charge of traditional composition is obstacle of effective use in multicell coke heaters. So, new type of coke-oven (shaft furnace) for coal charge with low coke yield was developed and tested in experimental-industrial variant. It is combined with processor for uninterrupted coal treatment with reagents. Its test result allowed to calculate, that prime cost production of 1 ton blast-furnace coke according new technology will be as 15-20% as less than on traditional one.

It is possible to use developed technology at existing coke plants without any changes in production process. Increased plastic properties of treated coals allows to add lean coal and rise coke yield up to usual level. In this case the plant will get additional profit thanks to exchange of expensive coals by cheap ones.

Resources of wastes for solvents-reagents are more than 200 million tons per year, it allows to introduce into coke industry about 400 million tons of lignite and candle coal

and 100 million tons of lean coal. Therefore, introduction of new technology will allow to obtain 350-400 million tons of coke, 200-150 million tons liquid hydrocarbons and 150-175 billions m³ of gas annually.

RESUME:

1. Chemical treatment of LMC in liquid phase with reagents and catalysts allows to obtain metallurgical coke .
2. Chemical treatment of noncaking coal increases coal plastic properties by means of chemical mechanism of their pyrolysis to generate LNS due to aromatic condensation promotion.
3. Sintering coal properties increase up to fat and coke coals allows to save expensive coals, use lean coal in coking charge and compensate low coke yield from LMC.
4. LMC chemical treatment process proceeds at atmospheric pressure and moderate temperature, therefore, could be involved into coke industry easily.
5. High yield of liquid small molecular weight by-products improves financial result of coking due to raw materials for motor fuel production.
6. Developed equipment for chemical treatment allows to process non-liquid wastes and get addition profit due to involve cheap coal into coke production.

LIST OF LITERATURE:

1. A.V. Madatov, G.A. Vlasov, V.D. Barsky, G.G. Kleshnya // About Colloidal Structure and Peptization of Coals with Melted Waste Plastics // Abstract Booklet of the Twenty-Second Annual International Pittsburgh Coal Conference "Coal – Energy, Environment and Sustainable Development". Pittsburgh, PA, USA, 12-15 September, 2005. – C.49.
2. A.V. Madatov, G.A. Vlasov, V.D. Barsky, G.G. Kleshnya // Colloidal Structure and Peptization of Coals with Melted Waste Plastics// Углекимический журнал, 2005, №1-2.С.10-16. ISSN 1681-309X.
3. . Vlasov G.A., Barsky V.D. //Metamorphism and dynamics of solid fuel composition// Углекимический журнал. – 2005. – № 1-2. – С.3-10. ISSN 1681-309X.
4. Vlasov G.A. //f Scientific basis and technology of chemical byproducts obtaining of coal thermal destruction// Thesis for a Doctor's degree, Lviv, Ukraine, 2005.