REDUCTION OF TAR FORMATION DURING COMBUSTION OF LIGNITE

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This article summarizes findings obtained during experimental laboratory pyrolysis of lignite from Československá armáda mine. The goal of the experiments was to find high volume additives, which are cheaply available. These additives would reduce undesirable formation of tar during lignite combustion in stoves and other local combustion chambers thereby leading to significant reduction of air pollution in the residential areas. The quantity of the additives ranged from 1.5 to 5 wt%, temperature of lignite pyrolysis was up to 580 °C. Heating process in the lignite pyrolysis during the course of combustion in the local combustion chambers was modelled. The additives selection followed REACH guidelines and conditions of consecutive accumulation of secondary energetic products. The best results out of 17 tested organic and inorganic additives were found for 70 AE and Ekobent bentonites. These additives are also the most practical for this purpose as they are exploited next to the lignite mine.

1. Introduction

The main topic of this study is reduction of tar that is released during the combustion of lignite from the Československá armáda (ČSA) mine (Czech Coal a.s. group) in stoves and other local combustion chambers. Potential tar reduction can lead to significant environment-friendly benefits as the local heatings are important source of the air pollution of the number of Czech agglomerations.

The article summarizes results of the model laboratory experiments of lignite carbonization up to temperature 580 °C with addition of selected additives. The additives had one of the three main roles: firstly, to limit the tar liquid substances formation from volatile lignite combustible matter, secondly, to retain them in solid substance, or thirdly, to transform them into the substances keeping them from negatively influencing the combustion process in the local combustion chambers.

This work was initiated by use of the already mentioned lignite for heating in the local combustion chambers and it follows-up on the experience gained during prior periods. On one hand, it searches for a solution of particular exploitation problem of the north Bohemia lignite from ČSA mine, on the other, hand it also answers general theoretical questions related to the issues of preconditions that it would not negatively influence the burning process in local combustion chambers.

2. Lignite pyrolysis and its mechanism

2.1. Lignite combustion

Lignite is throughout the burning process classified as a solid substance, which is succumbing the pyrolysis and heating process. In this manner, volatile gas sub-stances and solid pyrolysis residuum with high carbon content are created.

The quantity and structure of the gaseous products and residue depends in particular on the temperature and heating regime. The gaseous products are being combusted. Then volatile compounds are released from the solid pyrolysis residuum and they get oxidized. Both processes happen simultaneously many times [1-6].

Based on the thermodynamic calculations and tested data, it is possible to linearly formulate the relation of listed reaction enthalpy of reactions on the temperature [1].

This mechanism is initiated by absorption of oxygen during the formation of various adsorptive complexes [2].

Burn process of many solid combustibles is running through active complexes. It involves the diffusion, infiltration of the gases through pores and tears, adsorption, chemical reactions, desorption of the gaseous products and their diffusion into the ambient [3].

Considerably more complicated relations happen in cases, when both phases are moving. During the sufficiently low velocity of the gaseous phase toward the solid phase, the entire velocity is limited by exterior mass transfer. The velocity of the process depends on the velocity of the gas toward solid lignite phase and its character. It does not depend on porosity of the lignite [4].

In case the entire velocity is limited by internal mass transfer (molecular diffusion), the entire velocity is not dependent on the velocity of the gaseous phase towards the solid one, but is driven by the porosity of the solid phase, diffusion resistance of which increases with time [3].

2.2.   Primary products of lignite pyrolysis

The initial impulsion of lignite pyrolysis is transport of the heat from ambient into the lignite grain from the surrounding gaseous space or contact with the solid or liquid phase.

First of all, the exterior surface of the grain is heated. After, the transport of the heat into the centre of the grain follows. When the temperature is increased over the corresponding height, the particular chemical reactions progressively fluently start to run, which results into the primary products degradation of the lignite mass. These are being transported out of the lignite grains. The primary liquid products are summarily called primary tar. Primary products during the transport subject proximately further sequence of the following secondary reactions, which result into the gaseous, liquid and solid products – see Figure 1 [5].
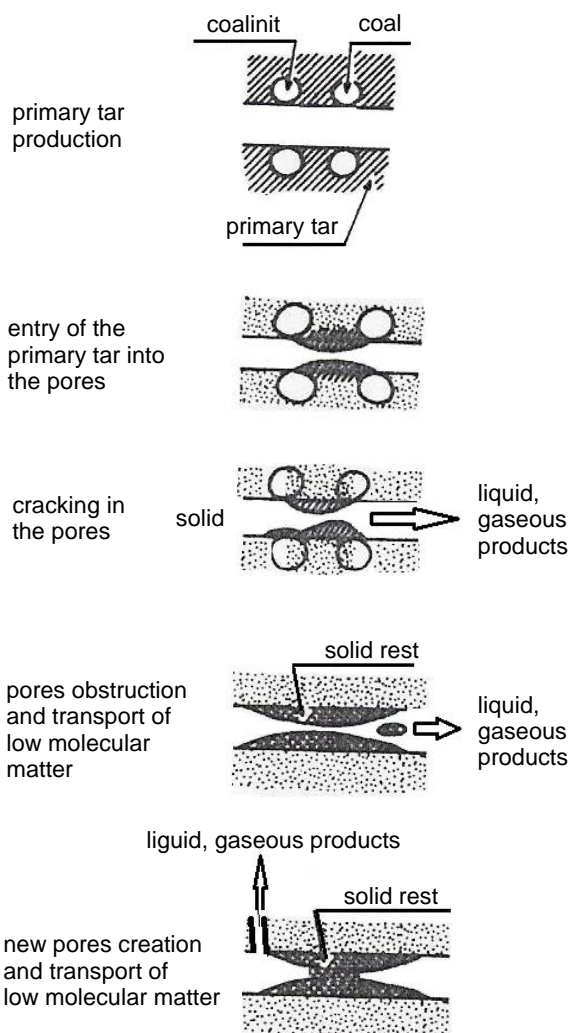

Fig. 1: Transport of primary pyrolysis products [5]

Mechanism of the thermal degradation of organic part of lignite mass supposes two tightly related processes – thermal depolymerisation of the lignite bitumen and thermal pyrolysis of the primary decomposition products.

Scheme on the Figure 2 demonstrates two possible types of primary thermal depolymerisation of the lignite mass. The lignite macromolecules are at first thermally activated – I. Activated molecules with the accumulated energy are stabilized by fission whereas the radicals are formed – II.
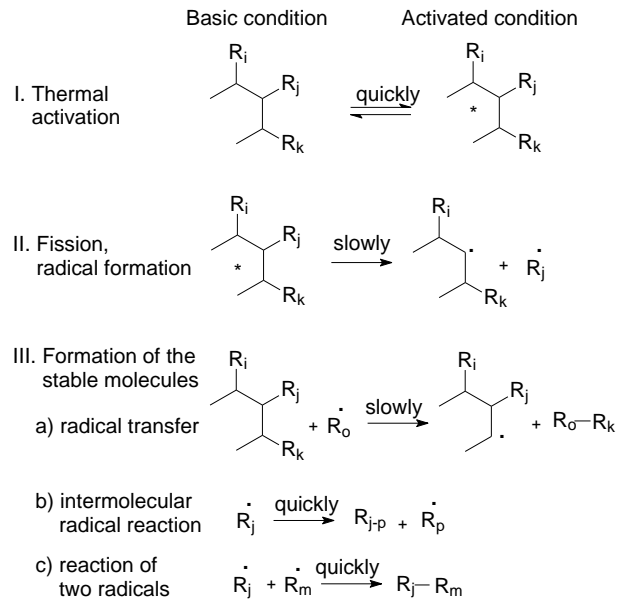

Figure 2: Thermal depolymerisation of the lignite mass [6]

The fission of the macromolecules happens in particular in the energetically weakest bonds, thus in the places of the least power consumption on the bond fraction. The weakest bonds in the lignite matter are alkylene ether and sulphide bonds [6].

The formation of the stable molecules from the large radicals proceeds through the radical chain mechanism – during the radical transfer, intermolecular radical reactions or by reaction of the two radicals. Main carriers of radicals are hydrogen and small hydrocarbons radicals.

The part of the ongoing fission reactions is also formation on condition, that pyrolysis no longer activates substances. Afterwards these solid carbon substances are burnt in the combustion chamber firing zone.

The goal of the research was to reduce the formation of the volatile organic substances by means of adding organic and inorganic substances. By that, we reduced their negative impact by dispersion of fumes on atmosphere in the ambient of the local combustion chambers. During this process, it is necessary to observe their impact on the manipulation with the respective additives as well as the quality of the secondary energetic products (SEPs) related to their possible use or more precisely their accumulation on the dumping sites [7-9].

2.3. Regulatory scope of manipulation with the SEPs

The SEPs accumulated in the unloading yards are in the EU level regulated by the regulations for handling the waste (directive 2008/98/EC, regulation no. 1013/2006/EC, decision 2000/532/EC, regulation no. 1357/2014/EU, decision 2014/955/EU) [7-9].

SEPs which come from the combustion process are used as additives for the construction masses or as the material for the backfills and filters. Considering this, they are products that have to be registered according the regulation REACH. There are 5 used kinds of SEPs registered under the following EC numbers: 266-046-0, 231-545-4, 231-900-3, 231-900-3, 297-049-5 in the Czech Republic.

When registering SEPs according to the REACH regulation, the producers had to provide the information about characteristic of SEPs and their toxicity. In total, there were 54 entries created. This process is motivated by expectation that the SEPs will be recovered and used once more e.g. in the construction industry etc. [10].

3. Experimental part

3.1. Selection of the experimental laboratory methodology

With respect to the problems related to the combustion of the lignite from the ČSA mine (calorific value 17.58 MJ/kg, ash 12.2 wt%, specific sulphur 0.53 g/MJ, water 26.8 wt%), low-temperature carbonization test was selected as the experimental comparing methodology. This methodology enabled evaluation of the examined additives reducing the tar formation.

3.2. Conditions of the experiment

The basic conditions of the experiment were taken from [11]. The backfill, with the respect of the retorts size, was about 20 g (the standard allows this backfill).

During the use of the examined additive in the solution, the lignite with the additive after mixing was kept in the room temperature minimally 48 hours. Evaluation of the quantity of the generating products respected standard conditions. This process for cases of temperatures and pressures applied in the local combustion chambers is schematically demonstrated on Figure 1.

However, the secondary reactions do not run only in the leaks of the lignite grains but also on their surface, in the space between the grains, as well as on the surfaces of the various temperature-resistant materials that limit the reaction spaces, on the surfaces of the solid components taken by flue gas from the combustion chambers, etc.

3.3. Temperature heating profile

Figure 3 shows the increase of the temperature during heating of the substances in the aluminium retort. This heating profile corresponds also to the temperature increase during the lignite combustion in the local combustion chambers.
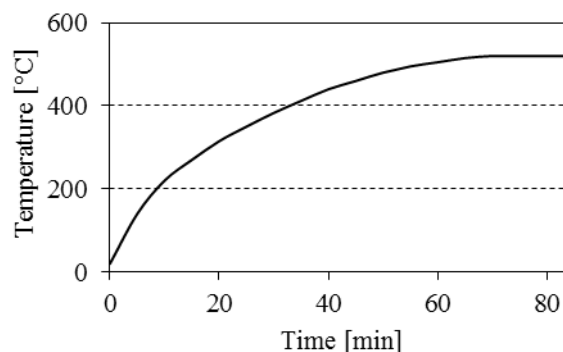

Figure 3: The actual process of the reactor temperature increase

3.4. The examined additives and their quantity

The additives that should reduce the tar quantity during the thermal lignite processing selected for our experiments are presented in Table 1. The selection was driven by on the data available and by our long term experience with the matter. Generally, two basic principles were followed during the selection:

1) Using the salts, we examine the loosening of tar substances into liquid and gas products of carbonisation. We investigated that through the creation of salts of organic compounds part the decay of organic part of lignin at low temperatures was reduced. During the selection of this group of additives, there was not left out the possible catalytic effect of some cations that are applicable during the lignite bitumen conversion.

2) The selected additives retain tar substances on their surface and then they reach the zone of the burn area of the local combustion chamber.

Price of the searched additive was also one of the important selection criteria. Other criteria included manipulability with the additive under the laid circumstances (especially in the winter months), respecting weight limitations due to expected household conditions and environment friendliness, in particular given by the legislation on the air protection against the polluting substances. We considered also manipulability with the possible secondary energetic products which will be generating clinker, ash or fly ash, during the possible future lignite with additive combustion and also possible future deposition in dumping sites.

The quantity of the additives to the lignite ranged from 1 to 5 wt%. The added additive weight to lignite in the laboratory conditions varied. The reason for this was the necessity of study the effect of the added component. The laboratory additives addition is summarized in Table 1. Most of herein listed substances are registered according the REACH regulation within EU ECHA that follows their characteristics, toxicity for human and environment. Most of them can also be found in the ECHA database where the possible risks are listed [5].

Table 1 Researched additives, their added weight and referential REACH registration number

Researched substance	Addition [wt%]	EC number
Active lignite	1	931-328-0
CaO	1.5	215-138-9
$NH_2CH_2CH_2NH_2.H_2O$	5	203-468-6
$FeSO_4.7 H_2O$	1	231-753-5
H_3PO_4	5	284-716-0
Zeolite – Klinoptilolite	1.5	…
K_2CO_3	3	584-08-7
Na_2CO_3	1	497-19-8
NPK[*)]	5	…
Urea	5	200-315-5
Charcoal	5	931-328-0
Bentonite – Ekobent	1.25	…
Bentonite – Keribent R	1.25	…
Bentonite – GAE	1.25	…
Bentonite – 70 NA	1.25	…
Bentonite – Sabenit	1.25	…

*) fertilizer NPK involves as the basic component potassium, as acid component phosphoric acid – see its „great" effect further on

4. Results and discussion

The effect of the additives was observed in particular by the quantity of the releasing tar, solid residue, water and gas, in conversion to the dry and wet lignite. Only the data concerning the tar that is visually - sedimentary separated from the water are summarized. [The part generating organic components soluble in water (phenols, thiols, etc.) was not evaluated in this work].

Due to practical reasons, it is better first to see the entire recorded range because this learning is important for eventual industrial use of the additives with regard to possible variability of the lignite composition. The ranges of recorded quantities of the crude tars are given in Table 2.

For the need of finding the data, it is better to assess the whole recorded range. This finding is then more useful for the possible usage in the industry. The averages of the measurements (each additive was monitored three times) for balance adjustments and in particular for easier comparison of the achieved data are given in Table 3.

In this table, it is also the ranking of the additives with regards of their effectiveness on reduction of the tar generated from the crude lignite during the low-temperature carbonization test.

When the data from Tables 2 – 3 are compared, it is obvious that most of the selected additives successfully reduced the quantity of tar released under the given laboratory conditions. Only potash, ethylene diamine and calcium oxide tend to facilitate the generation of the tarry materials during pyrolysis of the lignite.

Table 2 Quantity of the tar released during lignite pyrolysis with different additives

Additive	Tar [wt%]
Lignite	20 – 29
Active lignite	18 – 19
CaO	17 – 34
$NH_2CH_2CH_2NH_2.H_2O$	17 – 25
$FeSO_4.7 H_2O$	12 – 21
H_3PO_4	13 – 17
Zeolite – Klinoptilolite	12 – 22
K_2CO_3	14 – 28
Na_2CO_3	10 – 17
NPK	14 – 19
Urea	20 - 24
Charcoal	16 - 22
Bentonite – Ekobent	15 – 17
Bentonite – Keribent R	18 – 23
Bentonite – GAE	14 – 19
Bentonite – 70 NA	15 – 18
Bentonite – Sabenit	17 – 19

Table 3 Average quantity of the released tar and comparison of its quantity to the tar amount from lignite pyrolysis without additive and their ranking

Additive	Tar [wt%]	Comparison [%]	Rank
Lignite	24	-	
Active lignite	18	- 25.0	7 - 8
CaO	26	+ 8.3	16
$NH_2CH_2CH_2NH_2.H_2O$	21	- 12.5	14
$FeSO_4.7 H_2O$	21	- 12.5	13
H_3PO_4	15	- 37.5	3
Zeolite– Klinoptilolite	17	- 29.2	4 - 6
K_2CO_3	23	- 4.2	15
Na_2CO_3	15	- 37.5	10 - 11
NPK	17	- 29.2	9
Urea	22	- 8.3	12
Charcoal	18	- 25.0	7 - 8
Bentonite – Ekobent	16	- 33.3	1 - 2
Bentonite – Keribent R	17	- 29.2	10 - 11
Bentonite – GAE	17	- 29.2	4 - 6
Bentonite – 70 NA	16	- 33.3	1 - 2
Bentonite – Sabenit	18	- 25.0	4 - 6

Rem.: + increase of %, - reduction of %

In general, we can recommend adsorptive process of retainment of the forming tar on the surface of the active adsorbent with the consecutive combustion of the adsorbed substance (based on the observed complex of additives for solution of the observed problem). The most successful in this sense were Ekonent and 70 NA

bentonites. From other additives, good results were measured for GAE and Sabenit 65 zeolites.

Strongest reduction levels of the tar quantity recalculated onto wet lignite basis were recorded for phosphoric acid and soda. However, their price is rather high, especially in comparison with the bentonites. Additionally, manipulability of the phosphoric acid and soda is very problematic with regard to the disposition of the operation and installations of the majority local combustion chambers.

The amount of additives that was added to lignite was not based on detailed calculations and it is necessary to optimize it for existent local combustion chambers that use solid combustibles. However, when running these experiments, it is possible to focus on effects of lignite combustion with additives on walling of the combustion chambers, venting bodies, ash leach ability, etc., as well as on the emissive disposition of these combustion chambers. The cautious approach is needed especially when adding the alkali metal to lignite into the combustion areas, where in effect significant corroding process of the ceramic walling and encrustation rust formation could happen.

The total price of bentonites needed to attain the desired goal, i.e. reduction of the tar formation during combustion of lignite from the ČSA mine is fordable.

5. Conclusion

Our laboratory experiments with tar-reducing additives used in lignite pyrolysis showed that we were successful in finding several available high-volume substances that reduce tar quantity released during lignite combustion in local combustion chambers. The best results were recorded for Ekobent and 70 NA bentonites that are high-volume substances exploited next to the lignite source (ČSA mine). Both additives are economically acceptable and would be suitable for further testing in the following phase as additives to lignite during its combustion.

Their addition in amount of 1.25 wt% to lignite reduced the quantity of the released tar by approximately 33 wt%. The addition itself is economical and technically simply realizable process that can indispensably reduce the air pollution in the ambient of local combustion chambers in which the lignite from the ČSA mine is burnt. Application of both bentonites fully respects REACH guidelines as well as the conditions of the processing and accumulation of secondary energetic products.

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