

CHARACTERIZATION OF TAR DEPOSITS, EXTRACTION AND SORPTION PROPERTIES

Adrian Pryszcz, Barbora Grycová, Ivan Koutník, Veronika Blahůšková
VSB – Technical university of Ostrava, Institute of Environmental Technologies, 17. listopadu
15/2172, Ostrava-Poruba, 708 33, Czech Republic.
e-mail: adrian.pryszcz@vsb.cz, barbora.grycova@vsb.cz, ivan.koutnik@vsb.cz,
veronika.blahuskova@vsb.cz

Abstract

The main goal of this paper was to characterize and find a useful solution for the decomposition of tar deposits. For the experimental part, tar deposits, formed by polymerization and condensation reactions, were chosen from a storage tank for tars. At first the initial analyses of tar deposits (elemental, thermogravimetric, and calorimetric analyses) were performed. After the characterization, the tar deposits were extracted in the Soxhlet extractor by acetone, toluene, and quinolone and activated with potassium hydroxide. As the final step of this work, the sorption characterization on the 3Flex Surface Characterization Analyzer (Micromeritics) was performed. The specific surface area of the samples was evaluated using two methods – a single point measurement at $p/p_0=0.2$ and BET method. Micropore and external surface areas were calculated based on a t-plot analysis (carbon black model).

Keywords: Tar deposits, characterization, extraction, adsorption.

1 INTRODUCTION

Tar properties depend on the source of their origin. Most of tar is formed from a thermal conversion of coal (coal tar); the second part of tar is formed during pyrolysis or gasification of biomass. Due to efforts to use renewable sources of energy instead of fossil fuels, new technologies for pyrolysis and gasification are developed, especially for thermal processing of biomass [1-4].

Removal or conversion of tar is considered a technologically very challenging problem, because tar can condense or polymerize into more complex structures, which can lead to clogging pipes or heat exchangers. Tar elimination from the gasification product must be done before additional usage [5, 6].

Around 2.5 to 4.0 mass % of tar is obtained from the process of coal carbonization. Coal tar contains more high molecular compounds, than tar generated from biomass and it is an important source of aromatic compounds. From coal tar 15 to 25 % of BTX (benzene, toluene, and xylene) is obtained, 95 % of multi-ring hydrocarbon can only be obtained, and more than 90 % of anthracene, acenaphthene, pyrene, phenol, and most of heterocyclic aromatic compounds are gained. Nearly 100 % of carbazole, quinolone, and thiophene are from coal tar [7, 8].

Tar can polymerize, condensate, and form tar deposits. Nowadays tar deposits are characterized as a waste material and are mostly incinerated, therefore the main goal of this paper was to use tar deposits for preparation of activated carbon.

Activated carbons are produced from different organic precursors. The traditional production of activated carbon consists of two steps, carbonization and activation. The properties of the final product depend on the nature of raw material used and the activating agent [9-12].

2 CHARACTERIZATION OF TAR DEPOSITS

Tar deposits, formed by polymerization and condensation reactions, from a storage tank for tars were used for the experiment. At the start elemental, thermogravimetric, and calorimetric analyses were performed (with the use of the units LECO CHNS 628, TGA 701, and AC 600) to determine basic properties of the tar deposits (see Table 1). From the results it can be seen that tar deposits are high carbon based material with around 88 wt. % of carbon in dry sample and with a higher heating value of around $31 \text{ MJ} \cdot \text{Kg}^{-1}$. Around 6 wt. % of ash was in dry sample; therefore the next step consisted in determining the composition of ash from the tar deposits (see Table 2) with X-ray fluorescence (ARL QUANT'X EDXRF Spectrometer - Thermo Scientific).

Table 1: Elemental, thermogravimetric, and calorimetric analyses of tar deposits

C ^r (wt%)	H ^r (wt%)	N ^r (wt%)	S ^r (wt%)	O ^r (wt%)	W ^r (wt%)	V ^r (wt%)	FC ^r (wt%)	A ^r (wt%)	LHV ^r (kJ·kg ⁻¹)
70.33	2.28	1.07	0.55	0.27	15.30	35.21	44.21	5.28	31027
C ^d (wt%)	H ^d (wt%)	N ^d (wt%)	S ^d (wt%)	O ^d (wt%)	V ^d (wt%)	FC ^d (wt%)	A ^d (wt%)	LHV ^d (kJ·kg ⁻¹)	HHV (kJ·kg ⁻¹)
88.74	2.69	1.31	0.70	0.32	41.58	52.19	6.23	37600	31848

Table 2: X-ray fluorescence of ash from tar deposits

Si (wt%)	Al (wt%)	Fe (wt%)	S (wt%)	Ca (wt%)	Zn (wt%)	K (wt%)	Ti (wt%)	Mg (wt%)	P (wt%)	Pb (wt%)	Ba (wt%)
19.58	10.75	13.08	3.21	2.91	1.37	1.29	0.63	0.55	0.26	0.43	0.14
SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	SO ₃ (wt%)	CaO (wt%)	ZnO (wt%)	K ₂ O (wt%)	TiO ₂ (wt%)	MgO (wt%)	P ₂ O ₅ (wt%)	PbO (wt%)	BaO (wt%)
41.89	20.32	18.7	8.02	4.07	1.71	1.55	1.05	0.91	0.58	0.46	0.15

In the ash from the tar deposits, Si, Al, and Fe are the most abundant elements. The elements S, Ca, Zn and K are there in a lesser amount. The sulphur content of 3.21 wt. % is quite surprising as this means that sulphur is present in a form which will not burn at 900 °C.

3 EXPERIMENTAL PART

After the characterization, the tar deposits were extracted in the Soxhlet extractor, with acetone, toluene, and quinolone. The extraction was made to extract lighter hydrocarbons from the tar deposits. Such prepared extracted residues were activated with KOH. Approx. 15 g of sample was activated in a ratio of sample: KOH: distilled water 1: 3: 10, then the mixture was thermally treated in an inert atmosphere of nitrogen at 850 °C for 1 h. After cooling, the activated sample was neutralized with HCl, filtered and finally washed with water. The sorption characteristics were measured in the flow reactor and with the sorption of N₂ at 77 K.

4 RESULTS AND DISCUSSION

Two adsorption tests were made to measure sorption properties of the sorbent prepared from the tar deposits. First the sorption of selected VOCs (methyl ethyl ketone, isopropanol, toluene, and heptane) in the flow reactor was performed. The sample was first degassed at 350 °C and then approximately 0.1 g of sample was put into the reactor. Then the sorption and desorption properties were measured (see Table 3). The temperatures used for the VOCs sorption and desorption were: for methyl ethyl ketone - 41 °C, isopropanol - 50 °C, heptane - 56 °C, and toluene - 68 °C. For each VOC, the temperature corresponds to the relative pressure p/p₀ - 0.4. Each experiment was repeated 3 times.

Table 3: Sorption capacity measured in flow reactor of activated and non-activated sorbent prepared with acetone, toluene, and quinoline extraction from tar deposits

Name of prepared sorbent	acetone	toluene	quinoline	acetone act.	toluene act.	quinoline act.
used VOC	(wt. %)					
methyl ethyl ketone	0.67	0.74	0.96	12.73	13.69	11.65
isopropanol	0.19	0.19	0.39	4.84	5.65	5.03
heptane	0.57	0.37	0.77	8.59	6.71	8.00
toluene	0.38	0.56	0.48	9.77	9.72	8.19

The sorption of the selected VOCs for activated sorbents prepared by the extraction with acetone, toluene, and quinoline were very similar, but there was a big difference between the activated and non-activated sorbents. The activated sorbents could be used for the adsorption of VOCs.

The final characterization of the prepared sorbents was made by the sorption of N_2 at 77 K. The measurements were carried out on the 3Flex Surface Characterization Analyzer (Micromeritics). Approx. 1 g of sample for the non-activated samples and 0.1 g for the activated samples were used. The specific surface area of the samples was evaluated using two methods – a single point measurement at $p/p_0=0.2$ and BET method. Micropore and external surface areas were calculated based on a t-plot analysis (carbon black model).

Table 4: Surface areas of activated samples and non-activated sorbents

name of prepared sorbent	acetone	toluene	quinoline	acetone act.	toluene act.	quinoline act.
	$(m^2 \cdot g^{-1})$					
t-Plot Micropore Area	0	0	0	753	709	867
t-Plot external surface area	2	2	2	63	64	74
Single point surface area at $p/p_0 = 0.20$	2	3	2	794	736	885
BET Surface Area	2	3	2	817	772	941

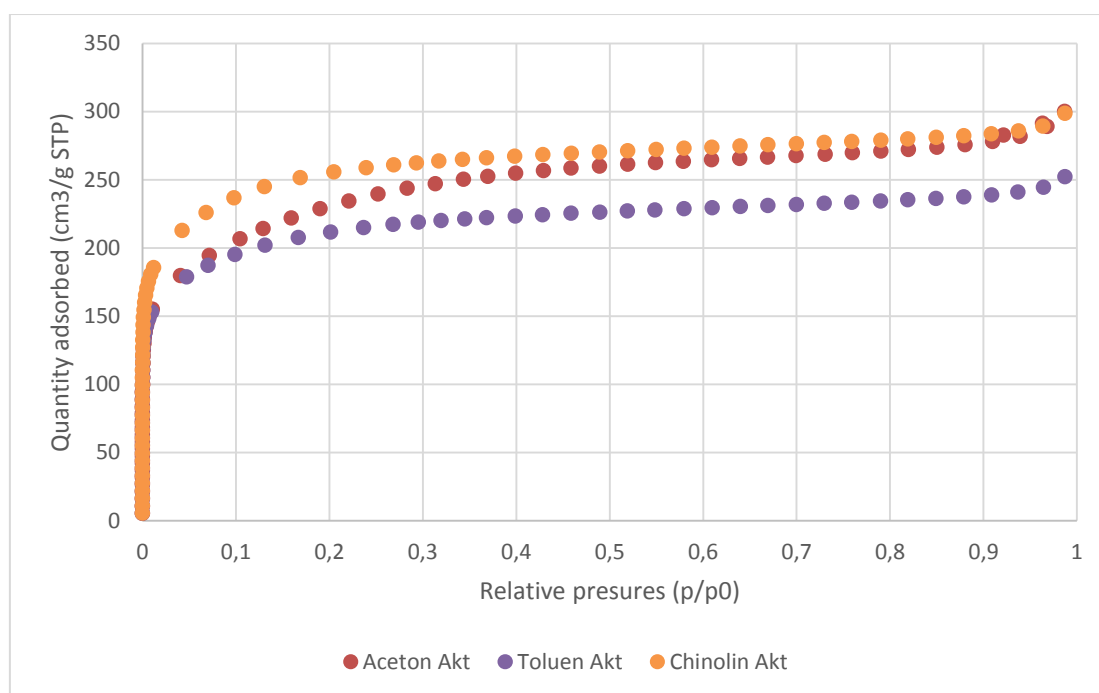


Figure 1: Adsorption isotherms of activated samples

The measured data from BET and t-plot confirm that the surface areas of the activated sorbents are similar, and they have sorption properties close to higher quality activated carbon (see table 4); the surface area of commercial activated carbons is in the range from 500 to 1500 $m^2 \cdot g^{-1}$. The non-activated samples have almost zero sorption properties.

5 CONCLUSION

From the laboratory results it can be concluded that tar deposits are high carbon based materials with around 88 wt. % of carbon in dry sample, with a higher heating value of around 31 $MJ \cdot Kg^{-1}$. The second part of the experiment was focused on the extraction and activation of tar deposits to create sorbents. From the comparison of the sorption properties for non-activated and activated sorbents, prepared by the extraction from tar deposits, it can be stated that the activated sorbents have a lot better sorption properties. The sorption properties depend mostly on well carried out activation; the selection of extraction solvent (acetone, toluene, quinoline) has negligible effect on the sorption properties. From the results it could be concluded that tar deposits, which are a waste material that is mostly incinerated, could be used for preparation of sorbents with a surface area of around 800 $m^2 \cdot g^{-1}$.

Acknowledgements

This article was created with the financial support of the student project VŠB-TUO SP2015/125.

REFERENCES

- [1] ŚWIERCZYŃSKI D., LIBS S., COURSON C., KIENNEMANN A. Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound. *Applied Catalysis B: Environmental*. 2007, **74**(3), 211-222.
- [2] LIU Y., HODEK W., VAN HECK K.H. Characterization of tar, char and gas from pyrolysis of coal asphaltenes. *Fuel*. 1998, **77**(9-10), 1099-1105.
- [3] JÍLKOVÁ L., CIAHOTNÝ K., ČERNÝ R. Technologie pro pyrolýzu paliv a odpadů. *Paliva*. 2012, **4**(3), 74-80.
- [4] HOLCOVÁ P., KALOČ M., 2006. Hodnocení vlastností pyrolýzních produktů z odpadní biomasy. In: *Úprava nerozpuštěných surovin*. Ostrava : VŠB TUO, 63-71. ISBN 80-248-1050-6.
- [5] CHUNSHAN L., KENZI S. Tar property, analysis, reforming mechanism and model for biomass gasification - An overview. *Renewable and Sustainable Energy Reviews*. 2009, **13**(3), 594-604.
- [6] ANISA S., ZAINAL Z.A. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. *Renewable and Sustainable Energy Reviews*. 2011, **15**(5), 2355-2377.
- [7] SCHOBERT H.H., SONG C. Chemicals and materials from coal in the 21st. *Fuel*. 2002, **81**(1), 15-32.
- [8] CHUNSHAN L., KENZI S. Resources, properties and utilization of tar. *Resources, Conservation and Recycling*. 2010, **54**(11), 905-915.
- [9] ESSER S., ANDRÉSEN J. M. Properties of Fuels, Petroleum, Pitch, Petroleum Coke, and Carbon Material. In: Totten G.E., Westbrook S.R., Shah R.J. *Fuels and Lubricants Handbook: Technology, Properties, Performance and Testing*. West Conshohocken, PA, USA: ASTM International, 2003, 757-786.
- [10] OTOWA T., TANIBATA R., ITOH M. Production and adsorption characteristics of MAXSORB: High-surface-area active carbon. *Gas Separation & Purification*. 1993, **7**(4), 241-245.
- [11] BUCZEK B. Preparation of Active Carbon by Additional Activation with Potassium Hydroxide and Characterization of Their Properties. *Advances in Materials Science and Engineering*. 2016, **2016**, <http://dx.doi.org/10.1155/2016/5819208>.
- [12] WUA M., ZHA Q., QIU J., HAN X., GUO Y., LI Z., YUAN A., SUN X. Preparation of porous carbons from petroleum coke by different activation methods. *Fuel*. 2005 **84**(14-15), 1992-1997.