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The Effect of Washing Oil Quality and Durability on the Benzol Absorption Efficiency from Coke Oven Gas

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Benzene, toluene and xylenes are mainly produced as by products beside metallurgical coke production. Absorption into the washing oil is of crucial importance in such technology. Washing oil is a complex mixture of hydrocarbons with higher boiling point and the washing property is changing during application period. Process parameter which is monitored as indicator of absorption process efficiency and washing oil condition is mainly concentration of unabsorbed benzene in coke oven gas outlet stream. Secondary parameter is viscosity of washing oil. The aim of reported study was verification of the optimal operating conditions of absorption unit of benzol and identify the ranges of physical properties (viscosity, solid phase content, surface tension and density) which mainly effects the process of benzol absorption. Beside the increasing absorption efficiency is significant extension of life cycle of washing oil, which makes the by-product technology more sustainable.

1. Introduction

Technology of metallurgical coke production is often accompanied by chemical by-product plant where coke oven gas is purified, and few chemical species are separated, Kozina, et al. (1973). Extensive review of coke making by-products with clarification of its basic properties and purposes of use is given by Tiwari et al. (2014). Ulyev et al. (2013) analyse process of benzene distillation and process of coal tar distillation which is typical for East European countries. The following oils are used for recovery of the benzol hydro carbons: petroleum wash oil (solar oil), coal wash oil, the heavy fraction obtained in the rectification of the still bottoms from the final rectification of crude benzol, and light medium oil. The degree of absorption of the benzol hydrocarbons from the direct coke oven gas as a function of the oil temperature and the gas and oil flow rates are typically examined. Selectivity of the process of absorption of benzol hydrocarbons from coke oven gas during a determined technological regime is demonstrated by Bezverkhii (1982). Coal wash oil is used in evaluated technology. Such type of wash oil contains typically naphthalene, acenaphtene, 2-methylnaphthalene, dimethyl naphthalene, fluorene, phenanthrene, anthracene, fluoranthen, pyrene, biphenyl, dibenzotiofen, carbazole, dibenzofurane and few other components whereas concentration of species is varying in time of wash oil lifecycle, Mathias (1931).

Heating of wash oil up to 200 °C and down to 25 °C is common part of benzol absorption-desorption process. Heating and cooling is quite rapid here and the wash oil passes it twice, occasionally three times per hour in reported process. Such large temperature change and presence of iron enhance creation of higher aromatic heterocyclic hydrocarbons which becomes solid and insoluble in low temperature conditions. On the other hand, the concentration of low molecular species such as naphthalene, methylnaphthalene, etc. is decreasing at the same process conditions. General information about coal chemistry is given by Speight (2016), details about chemistry of asphaltenes and chemical transformation during hydroprocessing of heavy oils are available in Ancheyta et al. (2017).

Presence of solid particles increase viscosity of wash oil, this together with decreasing concentration of lighter species has negative effect on benzol absorption efficiency. Solid particles are typically products of polycondensation reactions of washing oil components, which are often enhanced by impurities from coke oven gas, Weissermel and Arpe (1997). Technology of benzol scrubbing from coke oven gas may have a different solution, but the principle most of all remains the same Sowa et al. (2009). It is a physical absorption, when

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benzol is absorbed from coke oven gas into a washing oil, and afterwards is recovered by single-stage distillation. Engineering solution for design and rating calculations of absorption and distillation units are extensively given by Perry (2008). Partial regeneration of the wash oil is possible at the same time.
One of the possible technological arrangement is shown Figure 1. A saturated wash oil leaving benzol (BTX) scrubber is through storage tank pumped to the cold site of vapor cooler, where is currently preheated by the condensing vapor of benzol, which leaving the distillation column as distillate. Subsequently, it enters to the heat exchanger, where it is further preheating step. There is heat of the stripped washing oil available. Subsequent heating to the final distillation temperature takes place in steam preheater where 1.8 MPa of steam are usually supplied. The currently underway steam distillation, the head of the column leaving the vapours of water and benzol. They condense in the cooler. The condensate is separated and produced benzol is discharged for further processing. Stripped washing oil leaving distillation column from the bottom and is cooled in the exchanger, where the saturated wash oil coming from the benzol scrubber for first preheating step. It is further cooled in exchangers with water and continue back to the benzol scrubber for reuse.

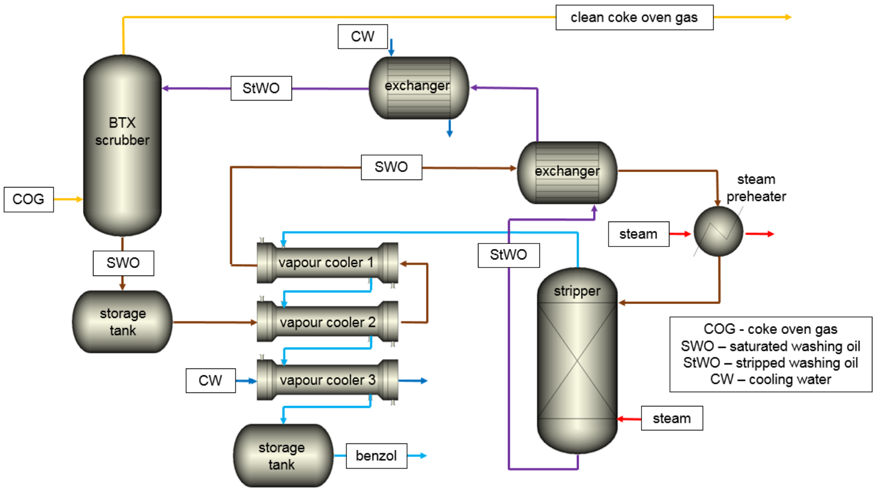

Figure 1: Technological scheme of benzol by-product plant.

This study is focused on monitoring quality of wash oil and on to determine key factors which effects losses and its application period. Trends of physical properties and chemical composition of wash oil enables optimization of coke by-product plant process condition and washing oil recharging intervals. Process data covering this study are taken from year operation period to eliminate effect of temperature changes during seasons.

2. Experimental

The benzol technology is the specific part of coke making by-product plant which was continuously monitored. Samples of original and used washing oil was picked at the defined time period during one operation season. The samples were supplied by the industrial partner, including the data on the supply of washing oil and the total oil changes in the circulation loop. Following physical and chemical properties of washing oil was monitored: viscosity, surface tension, density and solid phase content. Moreover, the impact test was carried out to simulate wash oil degradation in laboratory limited conditions.

2.1 Viscosity

Dynamic viscosity was determined on rotational viscometer Haake RS100 with configuration of coaxial cylinders Z40 DIN. Measurement was performed in controlled shear stress mode. Tests were performed at temperatures of 20 °C, 25 °C, 30 °C and 40 °C which are the most common temperatures when oil is in cool state, and when the viscosity is the highest.

2.2 Surface tension

The surface tension was determined by the method of Du Noüy (Lyklema 2000) using Krüss K100 static tensiometer. A sample of the wash oil was insert into a glass vessel and placed into an instrument where the surface tension between the liquid and the ambient air was determined. The determination was made by tearing off the Pt-Ir ring from the liquid surface, which is a standard sensor for the Du Noüy method.

2.3 Solid phase content

Sample of wash oil was extracted in xylene and insoluble solid content was measured. Insoluble residua were filtered by vacuum filtration and dried solid phase was weighted. Solid phase content has a great influence on viscosity of wash oil samples.

2.4 Impact test

The aim of the impact test was to monitor effect of impurities on the aging of wash oil. Long-time exposition at high temperature and individual saturation by ammonia and hydrogen sulphide was carried out in laboratory high pressure autoclave. The temperatures of 170 °C and 260 °C was chosen with respect to the process conditions in the benzol stripping column and in the tar column which can be eventually used as a regenerator of wash oil. Exposition was chosen to match the period of residence time of the wash oil in the benzol stripping column. Iron oxide was added to one set of samples to simulate effect of typical solid impurities in the benzol scrubbing process. After the wash oil sample exposition, the kinematic viscosity was measured by the Ubbelohde capillary viscometer.

2.5 The effect of temperature on absorption of benzol

The efficiency of absorption depends on the temperature of coke oven gas as well as on the temperature of the wash oil. The temperature of both media has a decisive influence on the quality and amount of the produced benzol. In principle, the higher temperature of the media decrease level of saturation of the wash oil by benzol. Equilibrium concentration of benzol in coke oven gas behind benzol scrubber is higher at the same conditions, thus the losses of benzol in the end gas are greater too. At temperatures below 15 °C, the viscosity of the washing oil increases considerably, and makes the pumping, distribution and passing through benzol scrubber difficult. At low gas temperatures, the naphthalene may solidify in the benzol scrubber and induce undesirable increasing of scrubber pressure drop. The optimal absorption temperature in such technology is 25 °C. In technological operation is necessary to keep temperature of wash oil slightly higher (1 - 3 °C) then temperature of coke oven gas, to avoid condensation water from the coke oven gas and its transfer to the washing oil. Wash oil containing significant amount of water creates a foam when benzol is stripped (Kozina et al., 1973).

3. Results and discussion

3.1 Viscosity

A flow curve was determined for each tested sample of wash oil. The Newtonian behaviour occurs at all tested samples measurements, it means there is constant viscosity at constant temperature regardless of whether it flows slowly in the pipeline or quickly on filling the BTX scrubber.

Viscometric tests were carried out at four temperatures (20 °C, 25 °C, 30 °C and 40°C). The resulting viscosities are pointed out at Figure 2. The temperatures are distinguished by colour. The results show that the viscosity of tested samples decreases with increasing temperature. There is also significant increase of viscosity with increasing time of application in scrubbing process. Experimental data cover three periods of wash oil refiling, which corresponds with obtained Viscometric trends.

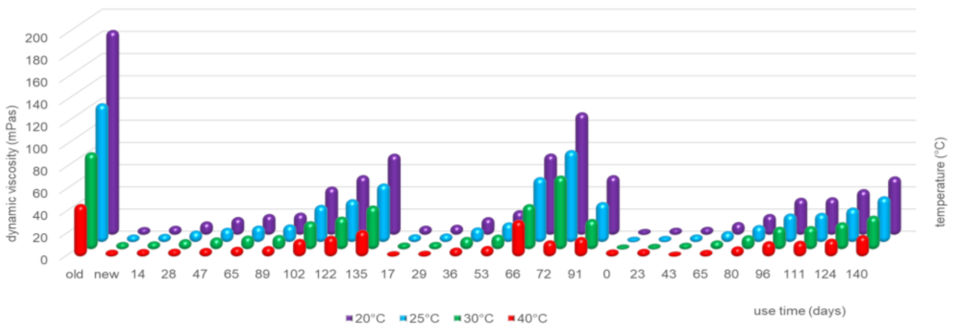

Figure 2: Dynamic viscosities of fresh and used washing oils at four temperatures.

3.2 Solid phase, density and surface tension

The solid phase content and density of washing oil samples are shown in Figure 3. Solid phase increases together with increasing of time of use. The same trend can be seen for densities of washing oil samples. The

maximal content of solid phase is nearly 18 % by weight. It is reasonable to assume that the proportion of solid phase substantially influences the viscosity of the washing oil at all temperatures.
Contrary to the effect of solid phase content on the viscosity and density, the effect of solid phase on surface tension of tested samples was not detected. The surface tension between all measured samples of washing oils and ambient air was nearly constant value.

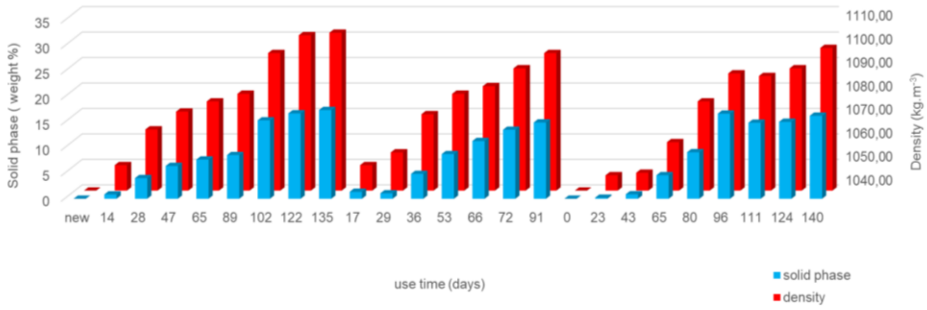

Figure 3: Trends of density and solid phase content in washing oil samples. Primary axis is for solid phase content, secondary axis is for density.

3.3 Effect of solid phase on viscosity of washing oil

The viscosity of dispersions is first of all controlled by the continuous phase liquid which might itself be Newtonian or non-Newtonian, and then the added dispersed phase where the size, shape, amount and deformability of the particles of dispersed material can vary considerably, as can the interaction between the individual dispersed particles. Although much empirical progress had been in the study of dispersion, the first theoretical work was done by Albert Einstein at the beginning of last century. (Barnes et al. 1989).
Exponential effect of solid phase on viscosity of washing oil shows Figure 4.

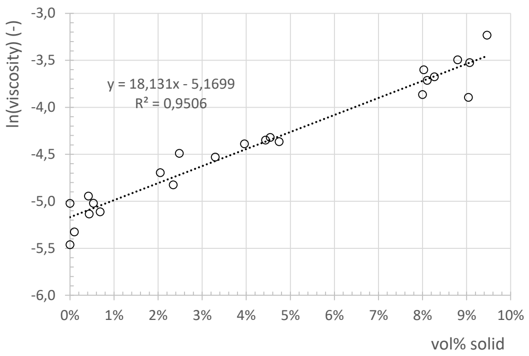

Figure 4 Effect of solid phase on wash oil dynamic viscosity.

The increasing amount of solid phase increases the viscosity of the washing oil. Stabilization of the viscosity is possible by continuous separation of solid phase, which cause extension of lifecycle of washing oil without significant changes to washing ability.

3.4 Impurity impact test

The results of the impurity test are shown in Figure 5. Increase in viscosity of the washing oil during its long-term heating is evident. All tested impurities applied this experiment have positive effect on increase of viscosity of the washing oil after long-term heating. The maximal effect occurs when ammonia is applied. On the other side minimal effect on increasing viscosity was detected for samples enriched by ferric oxide. All detected experimental trends show a nonlinear accelerating increase in viscosity.
An additional experiment conducted at higher temperature showed that increasing temperature also accelerated the formation of high molecular weight substances degrading its rheological properties, see Figure 6. The results show that contact of washing oil with ammonia and hydrogen sulphide together enhancing polycondensation reactions which cause creation of solid phase, especially in higher temperature (260 °C).

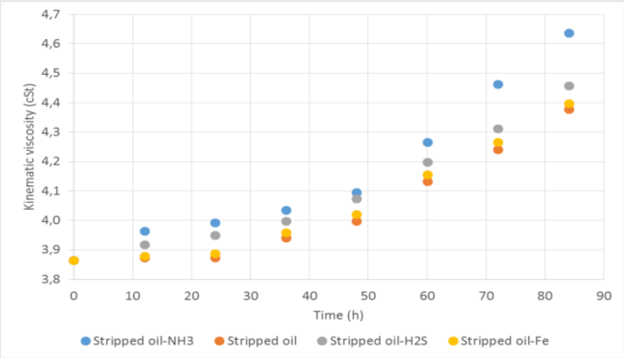

Figure 5: Effect of impurities on viscosity of stripped washing (tested temperature 170 °C).

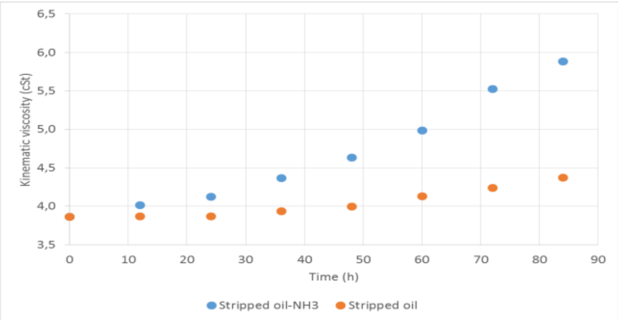

Figure 6: Impurity test in higher temperature 260 °C.

3.5 Saturation pressures and temperature

However, the wash oil is a liquid with a low saturated vapor pressure, also this property is strongly dependent on temperature. The saturation pressures for the individual wash oil components at the temperatures of benzol scrubbing process are shown in Figure 7. As one can see, the pressure of the saturated vapours of the more volatile components increase significantly with increasing temperature even in that narrow temperature range. If the percentage increase is expressed, when the basis of the saturated vapour pressure is at the optimum operating temperature in the benzol scrubbing column (25 °C), it is 32 %, 87 %, resp. 162 % of naphthalene with every 5 °C increase of wash oil temperature.

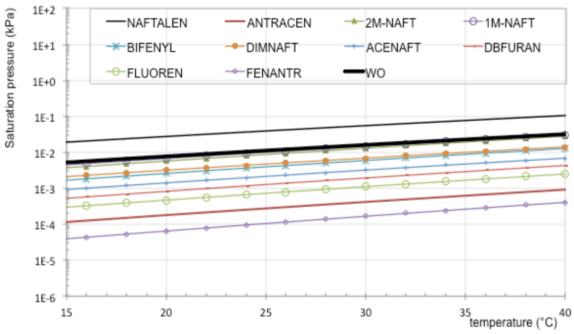

Figure 7 The saturated vapor pressures of major components of wash oil used for benzol scrubbing.

It is clear that the operating temperature of the benzol scrubber must be strictly controlled to reduce the losses of wash oil by evaporation into the coke oven gas. At lower temperature, the saturated vapor pressure of the wash oil is lower too and the evaporation to the coke oven gas is lower.

In practice, this means keeping the temperature of the coke oven gas at the entrance to the benzol scrubber. In the wider context of desulphurization of coke oven gas, the temperature of the coke oven gas must also be monitored by hydrogen sulphide and ammonia strippers.

4. Conclusion

Process of benzol scrubbing and stripping was monitored. Physical chemical properties of wash oil was measured with respect to operation condition to determine main factors effecting efficiency of benzol scrubbing and losses of was oil.

The temperature of wash oil is a key parameter for monitoring the absorption as well as for the desorption efficiency of benzol. The benzol scrubbing process follows the scrubbing of hydrogen sulphide and ammonia from coke oven gas. Statistical evaluation of long-term trends of process conditions shows, that temperatures of the individual media are just on the upper edge or higher than recommended technological values. Higher temperatures of washing media decreases efficiency of absorption generally. Intensive contact of hydrogen sulphide and ammonia with wash oil has also enhancing factor to the degradation of the washing oil. Therefore, keeping optimal temperature regimes in all employed scrubbers in technology is of crucial importance. There is a significant loss of wash oil, caused by the lifting droplets into the gas and by the enhanced evaporation caused by the higher operating temperature of the absorption. Wash oil losses caused by evaporation can be roughly estimated from Figure 7. It can be seen that if the absorption is carried out at the optimal temperature of 25 °C, wash oil losses can be significantly reduced. Optimal operating temperature for the benzol absorption technology is associated with sufficient cooling of coke oven gas and the stripped wash oil.

Second factor reducing scrubbing efficiency is gradual degradation of the quality of the washing oil namely increasing amount of solid phase which dramatically increase viscosity of wash oil. Polycondensation reactions are responsible for relevant production of a dispersed solid phase. Regular temperature changes of wash oil during process (absorption ~30 °C and stripping process ~200 °C) certainly contribute to these types of reactions. Such temperature regime is standard in optimal operating condition. Further oil degradation occurs when it comes to contact with coke oven gas which contains too much hydrogen sulphide and ammonia. Concentrations of these substances in coke oven gas need to be lowered as much as possible, not only with regards to benzol scrubbing, but also due to ever-increasing environmental quality regulations. Better prewashing of these substances is conditioned by process control and by adjusting in particular the temperature regime in the ammonia and hydrogen sulphide scrubbers. Longer contact of washing oil with ammonia and hydrogen sulphide enhancing polycondensation reactions and thus enhance creation of undesirable solid phase. Extension of washing oil life cycle is possible by removal of undesirable solid phase. It is possible by the standard mechanical processes such as filtration or decantation or by partial rectification at temperatures above 200 °C.

Acknowledgments

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