

EXPERIMENTAL INVESTIGATIONS ON BIODIESEL AS AN ALTERNATIVE ABSORBENT FOR THE RECOVERY OF AROMATIC HYDROCARBONS UNDER INDUSTRIAL CONDITIONS

Michael Th. Müller¹, Holger Thielert², Diethmar Richter², Jens-Uwe Repke¹, Günter Wozny¹

¹ Berlin Institute of Technology, Straße des 17. Juni 135, 10623 Berlin, Germany

² Uhde GmbH, Gas Treatment Plants, Friedrich-Uhde-Straße 15, 44141 Dortmund, Germany

Abstract

The recovery of aromatic hydrocarbons from coke oven gas is of great economic interest. Therefore experimental investigations on a promising alternative absorbent, biodiesel were carried out under industrial conditions with the aim of determining the performance and proving its applicability for the BTX-removal. For this purpose a mobile mini plant was constructed at the Berlin Institute of Technology and installed at the coking plant ZKS at Dillingen/Saar, where it was integrated into the industrial process and set into operation. Some of the main experimental results proving the applicability of biodiesel are shown in this contribution.

Keywords: Absorption, Coke-oven gas, Biodiesel, Crude Benzene, Mini plant

1. Introduction

The recovery of aromatic hydrocarbons from coke oven gas by an absorption/desorption process, represents among others, one stage of the gas purification at a coking plant. Coke oven gas (COG) is a highly caloric and valuable by-product that forms during the coking process. For economic reasons the aromatic hydrocarbons, particularly benzene, toluene and xylene (BTX) are separated from the coke oven gas by physical absorption. A schematic process flow diagram of the examined process is shown in (Fig. 1). The main equipment consists of an absorption and desorption column, whereas the desorption part further comprises a stripping and a distillation section for regenerating the washing fluid and purifying crude benzene, respectively. Traditionally, coal tar oil (CTO) or diesel oil is used as absorbent for the recovery of BTX-components. Both of them show certain disadvantages. CTO for example is a mixture of up to 500 different components. During the desorption process a loss of light washing oil components occurs which leads to an accumulation of heavier molecules. The light fraction of the oil has to be replaced steadily to guarantee constant conditions. Diesel oil is generally used where CTO is not available as absorbent and can cause the formation of solid particles which negatively affect the plant operation.

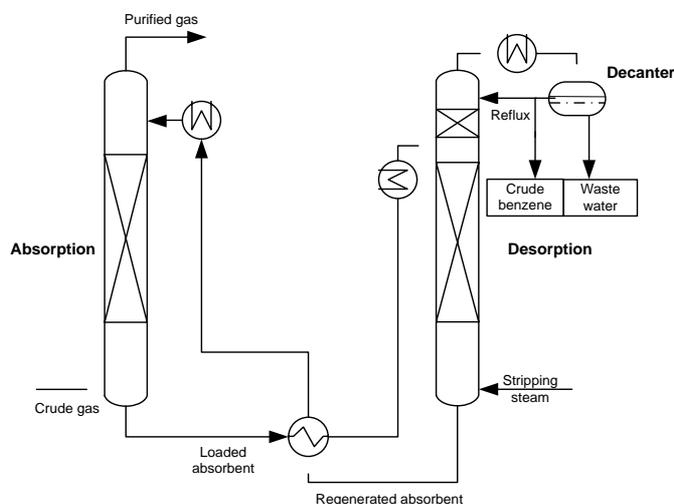


Figure 1. PFD-scheme of the BTX-recovery process

At the Berlin Institute of Technology biodiesel was discovered as a promising alternative absorbent for the recovery of aromatic hydrocarbons. Recent basic research under laboratory conditions showed, that the absorption capability can be increased up to 30% compared to CTO¹. By using biodiesel from rapeseed oil (rapeseed methyl ester – RME), a reduction of both investment and operational costs can be expected. Before introducing RME to industrial sized plants, further investigations have to be carried out under industrial conditions. It is of interest to gain experience using real coke oven gas in a steady state process in order to obtain basic process information such as absorption and regeneration capabilities and product qualities for different process parameters. After introducing the design of the mobile mini plant some of the main experimental results are shown and discussed in this contribution.

2. Design & construction of the Mini plant

Facing the requirements needed to carry out experimental investigations on a coking plant, a new concept for a mini plant was developed. For being most flexible the whole process was realised as a transportable plant module. The mini plant can be completely integrated into an industrial process with all incoming and outgoing process streams in order to produce raw benzene autonomously under steady state conditions. For the supply with coke oven gas and hot and cold utilities, certain interfaces were included in the process design (Fig. 2).

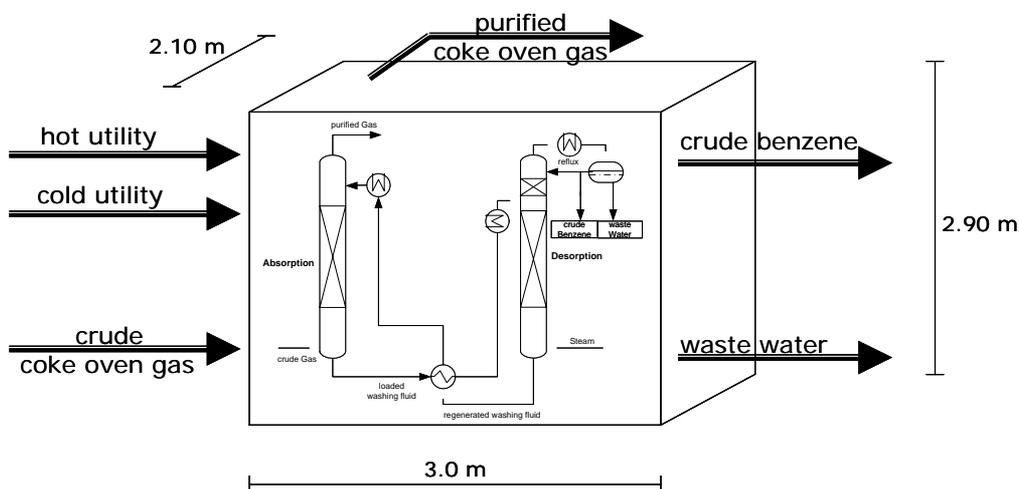


Figure 2. Interfaces and dimensions of the plant-module

Due to transportability the mini plant can be operated at different coking plant sites. The dimensions of the module, consisting of a stainless steel framing, were determined regarding the transport ability of the mini plant and are also shown in (Fig. 2). An existing computer model, validated against laboratory experiments², was used to prove, that an adequate absorption with the use of at least one meter of a structured packing is feasible. Thus, the absorption column was equipped with 1.5 meters of Mellapak 350. For the desorption column, Super-Pak 350 was used for the stripping and distillation part (1.0 and 0.5 meters), respectively. Further basic design parameters of the mini plant are shown in table 1.

Table 1. Maximum design parameters of the plant module

Absorption:		Desorption:		Rectification:	
Flow rate COG:	70 Nm ³ /h	Flow rate absorbent:	75 l/h	Flow rate product:	1.2 l/h
Flow rate absorbent:	75 l/h	Flow rate steam:	1.5 kg/h	Reflux:	0.8 l/h
F-factor:	1.6 Pa ^{0.5}	Gas to Liquid ratio:	20 kg/m ³	Reflux ratio:	0.4
Internals:	MellaPak350	Internals:	Super-Pak350	Internals:	Super-Pak350
Height:	1.5 m	Height:	1.0 m	Height:	0.5 m
Column diameter:	DN 100	Column diameter:	DN 100	Column diameter:	DN 100

Aspects of modularization and reuse were considered already in the planning phase as described in³. The whole mini plant module was constructed at the Berlin Institute of Technology (Fig. 3) based on a

3D-model that was drawn to effectively and efficiently place the main equipment in the framing. After configuring the process control system (Freelance 800F from ABB) first function testes were carried out before the whole plant-module was moved to the coking plant ZKS at Dillingen/Saar, where it was connected to the real plant and set into operation (Fig. 3). In order to guarantee a save operation of the mini plant, despite working with flammable and partly hazardous gases and liquids, strict safety regulations were implemented. Thus, the whole plant was built to meet demands on explosion protection regulation ATEX II2G. Furthermore a HACCP (Hazard Analysis Critical Control Point) Analysis was carried out to detect any conceivable safety gaps. An emergency shut down procedure was developed and implemented in the process control system.



Figure 3. Mini plant under construction (left) and in operation (right)

3. Experimental Setup

To gain the required information on the absorption capability of biodiesel, the mini plant is equipped with several sampling points for gaseous and liquid samples. At both bottoms of the absorption and desorption column, samples of the loaded and regenerated washing fluid can be taken. Furthermore the crude benzene quality can be monitored on a sample point, placed behind the decanter. To obtain information on the BTX-concentration of the entering and the purified COG stream, there are two more gas sampling tubes provided. The samples were analysed in a gas chromatograph (GC). Therefore four different GC-methods (for COG, crude benzene, loaded and pure RME) had to be implemented and calibrated. Each of the samples was analysed at least two times to get more precise and reliable results. Compared to the traditionally used washing fluid CTO, 99% of the biodiesel compound consists of 8 main components which all can be analysed and detected by gas chromatography. This additional advantage of RME allows the monitoring of the compound during the investigations additionally to the BTX-measurements. In the experimental investigation the following process parameters were varied, whereas each adjustment was controlled a by PID-controller:

COG Flow rate:	50 - 65 Nm ³ /h
RME Flow rate:	45 - 65 l/h
Steam Flow rate (Stripper):	0.8 – 2.2 kg/h
Desorber head temperature:	98 – 110 °C

In the three month of experimental investigation at the coking plant ZKS at Dillingen/Saar, up to 200 samples were analysed.

4. Experimental results

The aim of the experimental investigation was to prove whether biodiesel is an appropriate and efficient absorbent for the recovery of aromatic hydrocarbons also under industrial conditions. Two main targets were defined. At first, some basic research and observations on the behaviour of biodiesel as an absorbent in general were carried out. This will be discussed in 4.1. The second goal was to achieve some basic process data to demonstrate the superior performance of biodiesel. For all three main process units (absorption, stripping section and rectification section), characteristic parameters are shown in section 4.2 - 4.4.

4.1 Basic research

During the whole test period, a stable steady state operation without any disturbances was realised. At the beginning the process was started up and shut down every day. Later on, the mini plant was running up to 90 hours continuously. In summary the experience of 440 operating hours with coke oven gas was gained. Due to a higher recirculation rate in the mini plant, the attrition of the biodiesel can be compared up to 1.000 operating hours of an industrial sized plant. To get more detailed information on the behaviour of RME, the compound was analysed constantly by gas chromatography. Thereby it was from great interest if an accumulation of heavier components that are also absorbed from COG takes place, which may affect the absorption capability. Especially naphthalene is supposed to be an accumulating component. Thus, figure 4 shows the normalised concentration of naphthalene for the loaded and regenerated biodiesel over the total operating time, respectively. First of all it can be seen that no accumulation during time is taking place. The graph reveals that naphthalene can be separated by stripping the absorbent. The total concentration of naphthalene in the loaded and the regenerated RME is determined by the quality of regeneration, whereas the absorption ability of naphthalene (the concentration difference between loaded and regenerated absorbent) nearly remains equal. Depending on the amount of process steam, that is added to the stripping part of the desorption column, a better regeneration can be obtained.

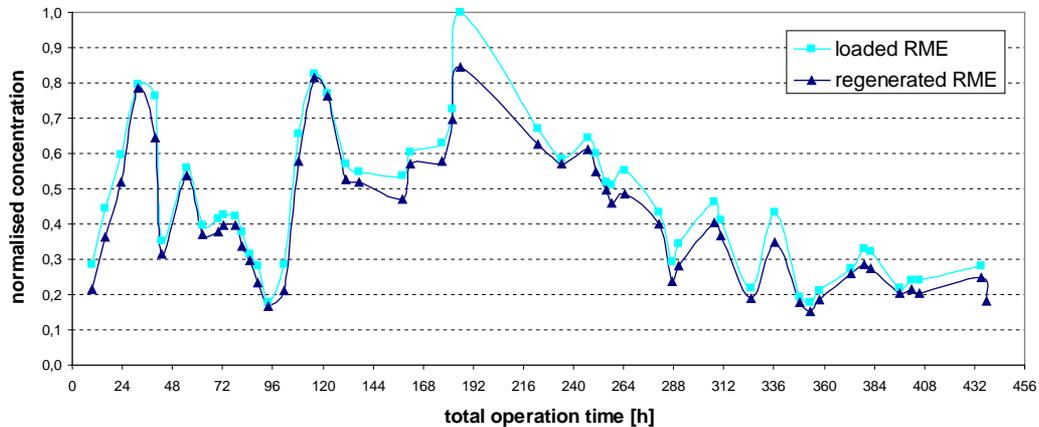


Figure 4. Normalised concentration of naphthalene dissolved in RME against operating time

4.2 Absorption capability of RME

One of the fundamental and most interesting information is the absorption capability of biodiesel under industrial conditions. Due to slightly different BTX inlet concentrations at the absorption column caused by variations in COG-production the recovery rate (RR) is introduced:

$$RR_i = \frac{c_{i,in} - c_{i,out}}{c_{i,in}} \cdot 100\% \quad (1)$$

According to equation (1), the difference between inlet and outlet gas concentration of the target component is based on the inlet concentration, which allows comparing different operating points. Another important parameter that characterizes the operating point is the liquid-to-gas-ratio (G/L-ratio) that expresses the amount of absorbent (in litres per hour) that is needed to purify one m³/h of COG. Figure 5 shows the trend of the recovery rate against the normalised L/G-ratio for the main target component benzene. The investigations were carried out for constant gas flow rates of 50 and 55 m³/h and a variation in the liquid load to gain the required L/G-ratio that correspond to industrial operating points. As it was expected, the recovery rate and with that the amount of dissolved benzene for higher L/G-ratios increases. Although only 1.5 meters of packings were used at the absorption column of the mini plant a recovery rate of up to 70% was achieved by using biodiesel as absorbent.

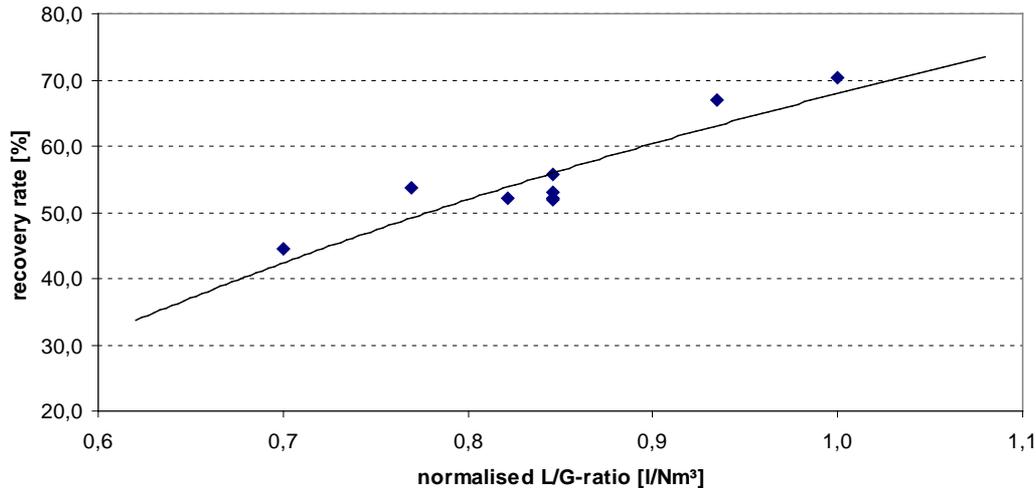


Figure 5. Recovery rate of benzene depending on normalised L/G-ratio

4.3 Regeneration capability of RME

For the regeneration of biodiesel, an important influence factor is the amount of steam [kg/h] that is needed for stripping one cubic meter of absorbent. The gas to liquid (G/L) ratio was varied during the experimental investigation. At the bottom of the desorption part the total amount of BTX components [mass-%] that remained in the absorbent was analysed. The results are plotted in Figure 6, depending on normalised G/L-ratio. By increasing the G/L-ratio, a better regeneration of the biodiesel is possible. Along the considered operating points, a linear dependency can be seen. Just like the absorption capability, the quality and efficiency of the separation strongly depends on the height and efficiency of the used internals. In this case 1.0 meter of Super-Pak 350 was used. However, the results show that a sufficient regeneration of RME is feasible.

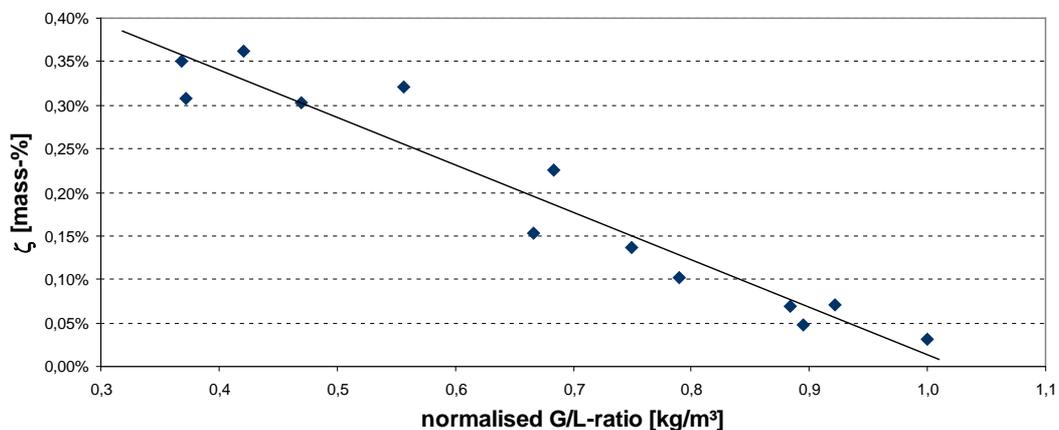


Figure 6. RME regeneration ability depending on the amount of stripping steam (normalised)

4.4 Quality of crude benzene

Besides the absorption and regeneration ability of biodiesel within the absorption process, the influence of the absorbent on the quality of the produced crude benzene is of great interest, too. Therefore the head temperature of the rectification part of the desorber was varied between 98°C and 110 °C by the reflux-ratio in order to identify the influence on product quality. The results are shown in figure 7, where the purity of crude benzene is pointed out in mass-%. As expected and indicated by the trendline, the product quality increases with lower head temperatures. In figure 7 a range of purity around 93 mass-% that is usually required in industrial applications is illustrated additionally. It can be seen, that head temperatures of up to 110°C are still matching the requirements compared to the traditionally used coal tar oil, where the maximum temperature is limited to 90°C. Increasingly light

components of CTO are stripped out at higher temperatures. This is leading to a reduction of product quality on the one hand and to a change of compound in CTO on the other hand. The compound of biodiesel and with that the thermodynamic behaviour remained almost constant throughout the whole testing duration which is a further advantage of the alternative absorbent.

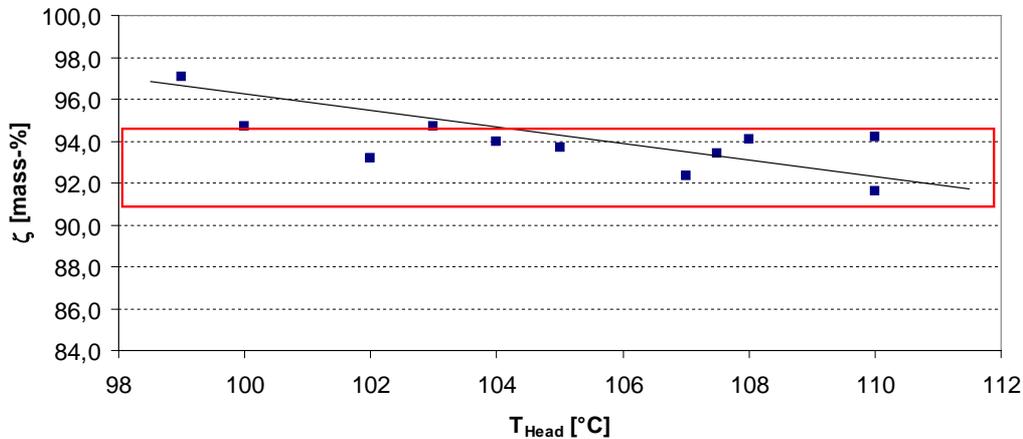


Figure 7. Product purity of crude benzene depending on head temperature

The benefit of using RME instead of CTO can be expressed in different ways. For an existing plant design, a lower reflux ratio is needed for producing the same quality or a higher product quality can be gained under remaining conditions, respectively. In case of a new plant design there are fewer separation steps needed for producing the same purity. This contributes to a reduction of investment costs for the plant.

5. Conclusions

For the purpose of the experimental investigations a mini plant was constructed at the Berlin Institute of Technology, installed at the coking plant ZKS at Dillingen/Saar and put into operation there. In 440 operating hours with coke oven gas in a steady state process of loading and regenerating the biodiesel, it could be proved that RME is a robust and efficient absorbent for the recovery of crude benzene also under industrial conditions. With 1.5 meters of packings recovery rates of benzene of up to 70% were achieved. Furthermore the application of biodiesel allows higher head temperatures at the rectification part for producing the same product quality compared to the traditionally used coal tar oil. This advantage additionally may contribute in lowering the operational and investment costs. Furthermore, additional experimental investigations will be carried out in order to compare both absorbents (CTO & RME) under similar conditions to point out the advantages of biodiesel and to quantify the benefit that can be expected by changing the absorbent.

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