MECHANIKA
CZASOPISMO TECHNICZNE
TECHNICAL TRANSACTIONS
MECHANICS
WYDAWNICTWO POLITECHNIKI KRAKOWSKIEJ
1-M/2012
ZESZYT 5
ROK 109
ISSUE 5
YEAR 109

ERIK ESCHE, DAVID MÜLLER, MICHAEL MÜLLER, GÜNTER WOZNY*,
JAN SCHÖNEBERGER, HOLGER THIELERT**

INNOVATIVE PRODUCT AND PROCESS DEVELOPMENT WITH MOBILE AND MODULAR MINI-PLANT-TECHNIQUES

NOWATORSKIE PRACE ROZWOJOWE NAD PRODUKTAMI I PROCESAMI Z WYKORZYSTANIEM MOBILNYCH I MODULARNYCH TECHNIK MINI-APARATURY

A b s t r a c t

For coke oven gas purification the removal of aromatic hydrocarbons is of great economic interest. In this contribution, feasibility and experimental studies on the applicability of biodiesel as an alternative absorbent to generate crude benzene under industrial conditions are presented. A flexible, modular, and transportable mini-plant was designed and built at Berlin Institute of Technology. The mini-plant mainly consists of an absorption and a desorption column allowing for the continuous loading and regeneration of the scrubbing fluid. After preliminary test runs, the whole mini-plant was connected to a coking plan. Subsequently, the modular mini-plant is modified and expanded for a more general application of an absorption and desorption process as CO_2 separation from various gases of the chemical industry or power plants is of interest. Especially with regards to flexibility, general design aspects are discussed.

Keywords: CO_2 separation, absorption, process design, modular constructions

S t r e s z c z e n i e

Usuwanie węglowodorów aromatycznych ma ogromne znaczenie ekonomiczne dla oczyszczania gazu koksowniczego. W artykule niniejszym przedstawiono wdrożeniowe i doświadczalne badania nad zastosowaniem biologicznego oleju napędowego jako alternatywnego absorbentu przy wytwarzaniu surowego benzenu w warunkach przemysłowych. W Berlińskim Instytucie Technologicznym zaprojektowano i zbudowano wielofunkcyjną przewoźną mini-aparaturę modularną złożoną przede wszystkim z kolumny absorpcji i desorpcji, co umożliwia ciągłe ładowanie i regenerowanie płynu przemywającego. Po przeprowadzeniu testu wstępnego mini-aparaturę podłączono do koksowni. W konsekwencji mini-aparaturę modularną zmodyfikowano i przeznaczono do szerszego zastosowania w procesie absorpcji i desorpcji, jako że oddzielanie CO2 od różnego rodzaju gazów w przemyśle chemicznym lub elektrowniach budzi dziś spore zainteresowanie. Omówione zostają ogólne aspekty projektu, zwłaszcza w odniesieniu do jego wielofunkcyjności.

Słowa kluczowe: oddzielanie CO2, absorpcja, projektowanie procesowe, konstrukcje modularne

* MSc. Erik Esche, MSc. David Müller, Dipl. Eng. Michael Müller, Prof. PhD. Eng. h.c. Günter Wozny Chair of Process Dynamics and Operation, TU Berlin.

** PhD. Eng. Jan Schöneberger, PhD. Eng. Holger Thielert, Uhde GmbH, Gas Treatment Plants, Dortmund.

1. Introduction

The removal of hydrocarbons from coke oven gas and the separation of carbon dioxide (CO_2) from various gases in power plants or chemical industry represent two of many applications for gas scrubbing processes, which are of scientific and economic interest. An application to investigate these two goals is discussed in this contribution.

Firstly, recent basic research under lab conditions at Berlin Institute of Technology has shown, that biodiesel is deemed to be an efficient alternative absorbent to generate crude benzene from coke oven gas. Compared to traditional absorbents (e.g. CTO: coal tar oil), biodiesel was found to increase the absorption capability by up to 30%. Moreover, by using biodiesel from rapeseed oil (rapeseed methyl ester), it is possible to further reduce investment and operating costs [2, 5, 6].

Secondly, CO_2 needs to be removed from various gas streams for a host of reasons: power plants need to limit their emissions, chemical plants want to further process a product gas stream and need to remove CO_2 beforehand, or want to extract it as a product itself. The state-of-the-art removal process for CO_2 from gas streams is an absorption using for example MEA or MDEA [7]. However, several other amine-based scrubbing liquids are being developed, which have been tested in lab environments, but not in many industrial applications.

The application of both considered processes requires the implementation of a combined absorption-desorption process for continually loading and regenerating the scrubbing fluid. In addition, some supporting pre- and post-processing steps are required for the continuous operation.

2. Challenge and solution approach

As all gas compositions in power or chemical plants may be subject to stronger fluctuations or contaminations and as it is difficult to simulate those in any lab environment, a mini-plant is required to test the operability and to prepare the next step towards the industrial application. The afore-mentioned variety of applications demands the transportability of the mini-plant, which needs to be considered during the construction of the plant. The subject of this contribution is the design of a mobile, modular mini-plant and its operation for extracting crude benzene from coke oven gas and the subsequent redesign of the same module into a flexible mini-plant for removing CO_2 from gas streams. Apart from the actual plant design various issues have to be faced, namely: operability, process, control, cost efficiency, safety, and hazard management; not all of which are discussed herein. With respect to cost efficiency the reusability of mini-plant process units is to be considered.

3. Design and application

By constructing mobile mini-plants the lack of operational experience before the actual industrial application can be rectified [7]. Ideally, a mobile mini-plant can be transported without any greater constructional efforts and connected via standardized interfaces to any industrial site. The lengthiest part of the set-up is reconnecting all cables to the process control system.

The following sections explain, how the plants for the two afore-mentioned processes were designed, what measures were taken to ensure safe operation despite the close proximity of the operator to the plant, and presents some details on the experience gained for coke gas cleaning.

3.1. Process design

The basic idea of both processes is quite similar. There are only some minor differences in pre- and retreatment of gas streams and the heat source for the regeneration of the absorbent. Fig. 1 shows a rough process flow diagram for the BTX recovery, (benzene, toluene, and xylene). The crude gas is injected at the bottom of the absorption column, where structured packings guarantee a large surface to the scrubbing liquid, i.e. biodiesel, which is introduced at the head of the column. The loaded scrubbing liquid or absorbent, which leaves the absoprtion column at the bottom, is preheated before being fed to the desorption column. Steam is used for the regeneration of the scrubbing liquid removing the crude benzene. In addition, the head of the desorption column is used for the additional rectification of the crude benzene, which is condensed after leaving the desorption column and separated from waste water in a decanter. The main purpose of the rectification is the reduction of the absorbent loss through the crude benzene. Based on lab experiments, a rate-based model for the coke oven gas purification using RME was derived [6]. The plant design of the BTX recovery is based on this model and the experiences gained during the respective experiments. Furthermore, the physical dimensions of the modular mini-plant and in turn the total height of all columns are restricted by the required mobility of the plant. This has to be considered for the actual design, which is meant to be 1:1000 the size of an actual industrial application, regarding the feed stream.

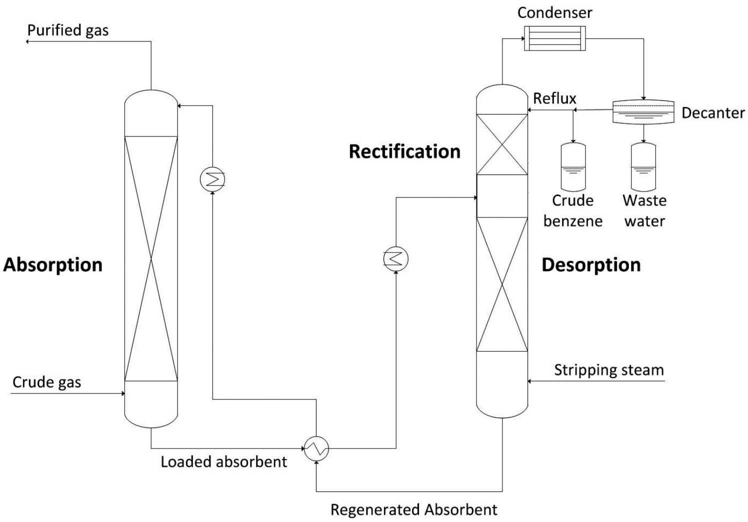

Fig. 1. Simplified process flow diagram for BTX recovery taken from [2]

Rys. 1. Uproszczony diagram przepływu procesowego dla odzysku BTX [2]

Despite the basically similar process, a number of adjustments need to be introduced for turning the BTX-recovery into a CO_2-absorption module. Fig. 2 shows a simplified process flow diagram for the flexible absorption of CO_2. Because of possible impurities in the crude gas, it is pretreated in a first column with structured packings using sodium hydroxide solution to especially remove acidic components. At the same time, the pretreatment column is employed to cool the crude gas down to temperatures below 50°C before entering the absorption column. An amine-based absorbent is used to separate the CO_2 from the pretreated crude gas. The stripping steam used in the BTX desorber is replaced by an electrical heating unit. The gas streams leaving absorption and desorption column may contain traces of absorbent. To reduce this quantity and to lower the temperature, retreatment columns circulating water through structured packings are used. Superfluous liquid is reinjected into the absorption desorption process. Table 1 gives an overview over all possible gas compositions, pressures, and temperatures of the feed stream as the mobile mini-plant is meant to be connected to a wide variety of power or chemical plants. These feed specifications necessitate one feature of the process concept: The feed gas can enter the absorption path at almost ambient pressure. Hence, a compressor is required for transporting the gas through the columns to the outlet.

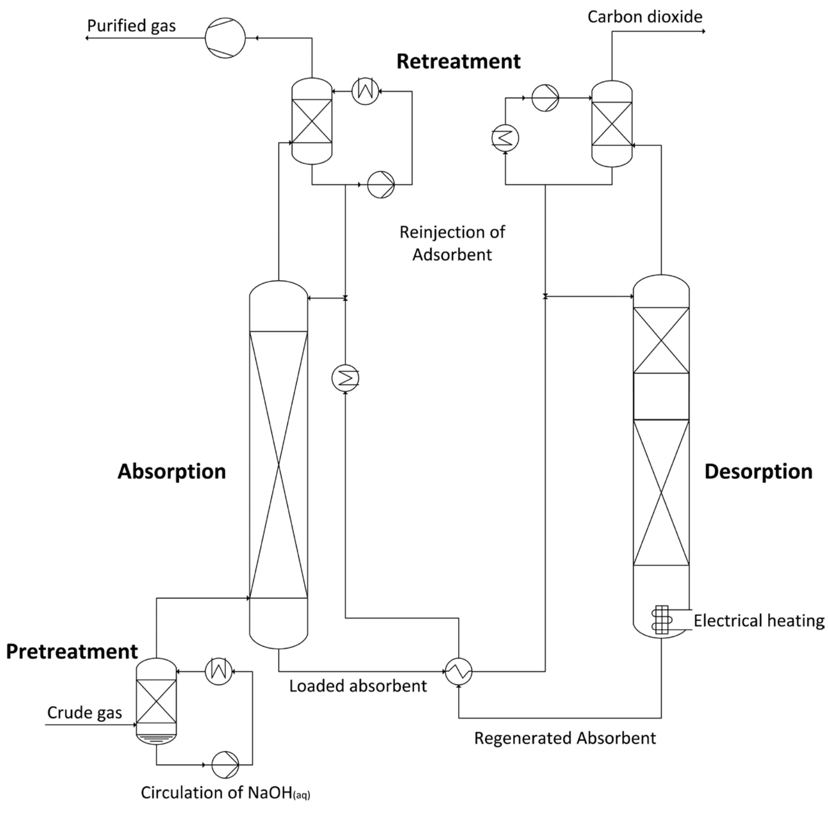

Fig. 2. Simplified process flow diagram for flexible CO_2-absorption

Rys. 2. Uproszczony diagram przepływu procesowego dla elastycznej absorpcji CO_2

Table 1

Considered gas compositions, temperatures, and pressures

Ranges	N_2	O_2	H_2	CO_2	CO	H_2O	p	T
	[vol%]	[vol%]	[vol%]	[vol%]	[vol%]	[vol%]	[bar]	[°C]
From	47	0	0	3	0	3	1,0	30
To	76	14	4	27	24	25	1,4	190

As it needs to be protected from corrosive components and spray water, it is positioned after the retreatment column and a set of filters and a receiver tank for retrieving liquid drops. Consequentially, the absorption is operated at 1 to 1.5bar, which is comparatively low. The same is true for the desorption column, where the elevated pressure is required to attain the desired temperature level. A control valve at the head of the column guarantees this.

For a preliminary estimation of the operation and design parameters, the process is simulated in Aspen Plus with MEA (monoethanolamine) and piperazine-actived MDEA (aMDEA, activated methyl diethanolamine) as absorbents to estimate the required number of theoretical plates for both absorption and desorption columns and the necessary heating duty for the desorption. Using the gas composition with the greatest quantity of carbon dioxide and requiring a CO_2 removal rate of 70%, the minimum number of theoretical plates for absorption and desorption were set to five and three respectively and the maximum power of the electrical heating unit was estimated to 8kW per 30Nm^3/h of feed gas.

3.2. Technical specifications and equipment planning

Based on the afore-mentioned simulations and experiences from similar applications, the geometrical, operational, and other technical specifications for both processes were chosen.

Fig. 3 shows a photo of the operating BTX module connected to the coking plant ZKS near Dillingen/Saar in Germany and the respective 3D model, which contains the most important aspects for the equipment planning. Piping for control air, inertization, and deaeration is left out. The thicker lines therein are all feed and clean gas pipes connected to the absorption column. Their diameter makes them bulkier than the other pipes, necessitating detailed planning of the piping. The only other pipe containing gas or vapour is the outlet of the desorption column to the condenser. The two cylinders in the center of the 3D model are the liquid feed tanks for the main columns. The BTX module is automated using ABB's Freelance 800F process control system. Over 60 temperature, pressure, level, and flow indicators provide information for controlling pumps, feed, cooling water, and steam flow rates. In addition, control sequences for automatic shut-down and inertization of the entire plant are implemented.

3.3. Modification of mini-plant to flexible CO_2-absorption

As has been mentioned before, redesigning the BTX process into a flexible mini-plant for amine-based CO_2-absorption requires some additional components. The three main challenges, are the confined space of the mobile module, the reusability of plant units for cost efficiency, as well as the adherence to the European directives on equipment and work in explosive atmospheres (ATEX).

The latter is mostly a funding issue, as ATEX equipment is usually more expensive and for many control or magnetic valves roundabout constructions using control air are required. To be mentioned in this context are the electrical heating units and the compressor. To implement the 10 kW electrical heating into the desorption column, two 5 kW custom build ATEX-certified electrical heating units are used. Both of which need to be completely covered by liquid during plant operation and consist of a bundle of heating rods which are 40 cm long. Therefore, a special bottom for the desorption column is built, which is roughly 50 cm wide and stands 80 cm tall.

This directly leads to the second challenge of the redesign: the confined space. The mobile module is 2.8 m high, 3.0 m wide, and 2.0 m deep. Given the addition of three new columns, namely the pretreatment and the two retreatment sequences, five columns in total have to be included in the module. On top of that, the compressor is added, which by itself requires 0.5 m^3 of space. To handle this issue a comprehensive 3D model is developed in AVEVA's PDMS containing all equipment and stainless steel piping. Fig. 3 shows the redesigned module both with and without the piping.

Obviously, rigorous planning is much more important here than in the first case. The columns in the 3D model are not accurate in size and most equipment in AVEVA is slightly larger than their actual physical counterparts. However, the main objective of the 3D model is

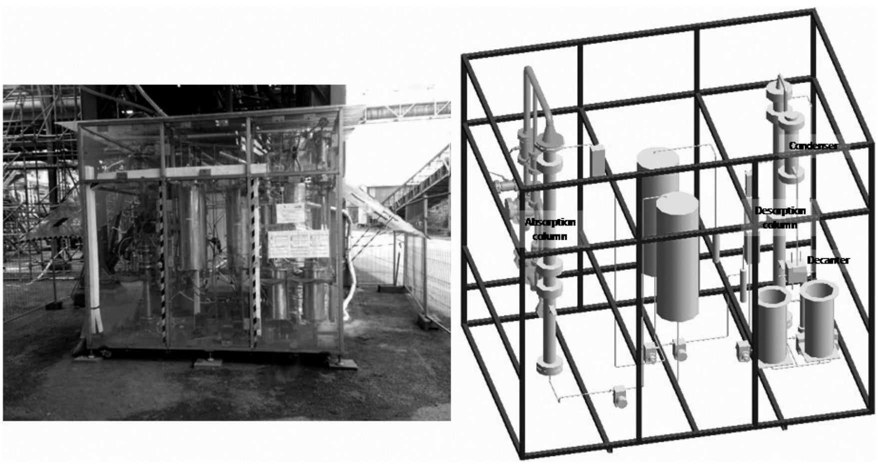

Fig. 3. Photo (left) and 3D model (right) of BTX module.
The mini-plant was connected to the coking plant ZKS at Dillingen/Saar, Germany

Rys. 3. Fotografia (L) i model trójwymiarowy (P) modułu BTX. Mini-aparatura została podłączona do koksowni ZKS w Dillingen (zagłębie Saary w Niemczech) to estimate whether all components can be fitted into the mini-plant and whether it can still be guaranteed to make all hand valves easily accessible and any other equipment attainable for maintenance. To protect it from leaking liquid, spray water, or else, a box is built around the compressor. At the same time this is meant to increase the accessibility of components only reachable from the center of the mini-plant. All predefined interfaces/connections are positioned at the back of the mini-plant on the left hand side, so that the entire plant can easily be protected with plexiglass panels against wind and rain on all sides. Some components, like the electrical heating units, need to be maintained more frequently or should not be inserted into the plant during transport. The flanges connecting the heating units to the desorption column's bottom are therefore positioned at the front side, so that they can easily be pulled out.

The third challenge, the reuse of process unit groups, has to be considered in all mini-plant constructions. The three additional columns are designed as triplets, thus reducing design and construction time. Furthermore, interfaces of the equipment are standardized for future reuse. This has already been taken into regard during the design and construction of the original BTX-recovery module. Given the similar process concepts most column parts and control structures can be reimplemented into the CO_2 absorption plant.

Originally, it was planned to use the programming of the process control system of the BTX process and to simply modify it. However, given the changed control structure, the number of additional components, and the consequentially new configuration of input and output cards, starting from scratch is the more sensible and less time-consuming approach.

Based on the feed specifications and simulations using MEA and piperazine-activated MDEA the height of packings in all five columns and the power of the electrical heating is somewhat oversized. This is meant to be a measure to heighten the flexibility of the mini-plant as it is not yet known which amine-based scrubbing liquids are going to be tested in the plant.

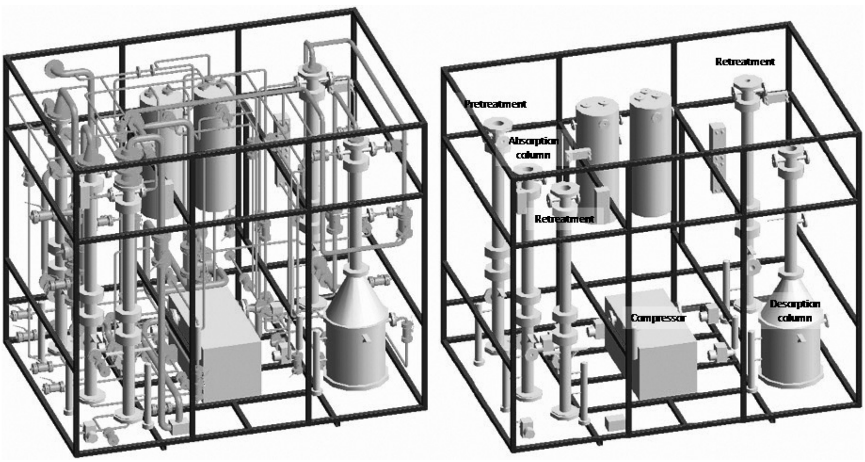

Fig. 4. 3D model of redesigned mobile mini-plant
with (left) and without (right) piping

Rys. 4. Trójwymiarowy model przeprojektowanej mini-aparatury mobilnej
z instalacją rurociągową (L) i bez niej (P)

3.4. Experience of coke oven gas cleaning

As the experimental studies on the coke oven gas purification have already been published elsewhere [2-6], the main findings will only briefly be revisited here.

During more than 440 operating hours, with a maximum of 90 hours between start-up and shutdown, coke oven gas of flow rates between 50 and 65 Nm^3/h was treated with RME circulating at 45 to 65 l/h. The steam flow rate was varied between 0.8 and 2.2 kg/h and the head temperature of the rectification part between 98 and 110°C. According to [2] this amounts to 1100 hours in an industrial size application.

Through stripping the RME with steam, the accumulation of naphthalene can be avoided and the regeneration improved. At liquid-to-gas ratios of roughly 1 l/Nm^3 up to 70% of the crude benzene contained in the feed gas can be recovered. At the same time, less than 0.05 wt% of crude benzene remains in the regenerated RME at the bottom of the desorption column. The desired product purity of 91 to 95 wt% can be achieved for head temperatures of 110°C and less. Using CTO as an absorbent this temperature was limited to 90°C, implying a higher reflux ratio. At the same time almost constant thermodynamic behavior is observed for RME, which shows a stark contrast to CTO, from which lighter components disappear with the crude benzene.

In total, the application of RME instead of CTO for the coke oven gas purification allows for both lower operating and investment costs as fewer separation steps are required. The stable operation in the mobile modular-mini-plant shows the industrial applicability of the process concept. Experience for the CO_2 removal has yet to be gained.

4. Conclusions

Through the construction of mobile, modular mini-plants, the void between lab experiments and the actual industrial application may be bridged. The deliberations in this contribution show this for the removal of aromatic hydrocarbons from coke oven gas and the CO_2 separation from various gas streams, which are both of economic interest for a possible industrial application. During the various stages of the plant design, operability and constructability have to be taken more into consideration than for any full-scale plant as the confined space, flexibility and uniqueness of the plant does not allow for full automation.

Hence, rigorous 3D planning of the equipment is required, especially with respect to the safety of the operator and ease of maintenance. The industrial viability of the BTX-recovery has already been successfully proven using the herein described mini-plant and shows promising potential for a large-scale application. Despite their uniqueness, modularization of applied equipment can help reduce design effort, construction time, and costs.

Abbreviations

ATEX – European directives on equipment and work in explosive atmospheres
BTX – benzene, toluene, and xylene
CO_2 – carbon dioxide

CTO – coal tar oil
aMDEA – piperazine-activated MDEA
MDEA – methyl diethanolamine
MEA – monoethanolamine
RME – rapeseed methyl ester

References

[1] Hady Ł., Wozny G., *Reuse-Atlas for know-how and quality-assurance in modular plant design*, Proceedings: 8th World Congress of Chemical Engineering, August 23-27, Montréal, Québec, Canada 2009.

[2] Müller M., *Experimental investigations on Biodiesel as an alternative absorbent for the recovery of aromatic hydrocarbons under industrial conditions*, Distillation Absorption 2010.

[3] Müller M., *Innovative Produkt- und Prozessentwicklung mittels mobiler und modularer Mini-plant-Technik*, Jahrestreffen der Fachgemeinschaft Prozess-, Apparate- und Anlagentechnik, Fulda 2011.

[4] Müller M., *On the applicability of Biodiesel as Absorbent for the Improvement of Aromatic Hydrocarbons Removal: An Industrial Application*, 2010.

[5] Richter D., *Absorption of aromatic hydrocarbons in multicomponent mixtures: A comparison of simulations and measurements in a pilot plant*, 18th European Symposium on Computer Aided Process Engineering – ESCAPE 18.

[6] Richter D., *Rate-Based and Equilibrium Model Approach for the Absorption of Aromatic Hydrocarbons in Multicomponent Mixtures*, AIChE Annual Meeting, Nov. 4-9, 2007, Salt Lake City 2007.

[7] Stünkel S., *Simultaneous Synthesis of the Downstream Process and the Reactor Concept for the Oxidative Coupling of Methane (OCM)*, 10th International Symposium on Process Systems Engineering, PSE 2009.