

# A NEW CONCEPT FOR CLEANING EXHAUST AIR FROM SOLVENT VAPOURS

Diana Ludgen, Hubertus Wichmann, Müfit Bahadir

Institute of Environmental and Sustainable Chemistry, Institute of Environmental and Sustainable Chemistry, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

**Keywords:** Air cleaning, differential thermogravimetry, exhaust air, solvent vapor, isotherms

## Abstract

Emission of large amounts of solvents with exhaust air from industrial production into the environment is a serious problem. In Germany, industry-sector-specific legal limit values are applied and technical measures for pollution reduction are required. Different techniques for exhaust air cleaning are in use but still posing problems concerning costs and reliability. For these reasons, the development of processes for exhaust air treatment is subject of current research. Here, a new concept for exhaust air cleaning is introduced that combines absorption of solvents by an organic fluid and the subsequent adsorption by molecular sieves placed in the absorber. It was managed to close the loops of solvent recovery and sorbents regeneration. In laboratory-scale experiments it was demonstrated that it was possible to reduce an initial ethylacetate pollution of  $800 \text{ mg/m}^3$  or  $349 \text{ mg C/m}^3$  below the limit value of  $75 \text{ mg C/m}^3$  for a 60 h duration. Thermogravimetric measurements assisted to define optimum conditions for solvent recovery at  $180 \text{ }^\circ\text{C}$  from the molecular sieve. One unexpected positive finding was that the solvent release was considerably increased by the presence of the absorption fluid while adsorption isotherms revealed first insight in this process.

## 1 Introduction

Today, public discussion is focused on carbon dioxide release as major cause of climate change and thereby as a symbol for air pollution. Outside the public perception, especially volatile organic compounds incl. solvent vapors strongly contribute to atmospheric pollution. Regarding global considerations of volatile organic compounds (VOC), methane is often excluded because it is emitted from natural sources, as well. In this context, the term non methane VOC (NMVOC) is in use. In the atmosphere under sunlight irradiation, NMVOC give rise to the formation of oxidants like ozone as well as nitrogen oxides, aldehydes, and organic acids [1]. According to the German Federal Environmental Agency, 52% of the entire NMVOC emission in 2009 consisted of solvent vapors [2]. This especially results from an extensive industrial use of solvents. The critical point in solvent application is the evaporation and transport via exhaust air into the environment, whereas in Germany industry-sector-specific legal limit values are applied [3]. Therefore, the reduction of solvent vapor emissions is mandatory.

Different processes for treating exhaust air are used in order to achieve emission limits. An overview of most common processes and their fields of application are given by table 1 [4-15].

Table 1: Common processes for exhaust air treatment and their fields of application

Process	Pollution level		Exhaust air flow		Regenerative	Emission limits achieved
	high	low	high	low		
Thermal oxidation	+	-	-	+	-	+/-
Catalytic oxidation	+	-	-	+	-	+/-
Biofiltration	-	+	+	+	-	+/-
Membrane technology	+	-	-	+	+	+
Adsorption	-	+	+	++	+	+
Absorption	++	-	++	+	+	+

++ well suited; + suited; +/- moderately suited; - not suited

Despite of the variety of the existing air treatment processes, only a few of them allow the recovery of the solvents. Furthermore, the processes are generally expensive and a reliable continuous operation is difficult to realize in practice [16]. For these reasons, development of efficient and economic processes for exhaust air treatment is subject of current research [17-19]. In this context, the concept of a novel combined absorption/adsorption process for exhaust air cleaning from solvent vapors is introduced in the following that enables recovering all components involved.

## 2 Materials and Methods

### 2.1 Construction of a lab-scale experimental unit

The laboratory-scale exhaust air cleaning unit consisted of two 2 L flasks containing the solvent and the absorber fluid, two flow control units for nitrogen, a glass bridge connecting the flasks as well as a hose pump for the absorber fluid and a column (length: 100 cm, i. d.: 7 cm), filled with Raschig rings (0.5 cm). Air cleaning was achieved by uptake of the gaseous solvent into the absorber fluid, applying the counter flow principle. In the unit, the active absorbing surface was 2.45 m<sup>2</sup>. For continuous cycling, the absorber fluid was pumped from its reservoir to the column head. For this, the fluid was taken from the bottom outlet of the reservoir flask, below a layer of molecular sieve granulate (molecular sieve 1 nm, Merck; SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Faujasit structure, pore size: 1 nm, granulate: 2-3 mm, surface (BET): 636 m<sup>2</sup>/g). The production of the solvent vapor was achieved by passing a stream of nitrogen 10 mL/min through the solvent reservoir. A second stream of nitrogen above the solvent containing flask was directed towards the glass bridge and the column. The total gas stream adjusted in all experiments amounted to 500 mL/min. In this way, a solvent concentration of 6 g/m<sup>3</sup> was generated which in industrial practice would stand for a quite high air pollution. A lower solvent concentration

of  $0.7 - 0.8 \text{ g/m}^3$  was achieved by cooling the solvent reservoir to  $10 \text{ }^\circ\text{C}$ . For the experiments that are described here, ethylacetate (SupraSolv, Merck) was used as air pollutant and biodiesel (Connediesel, ADM Hamburg AG) was applied as absorber fluid.

## 2.2 Gas analysis

For gas sampling, glass tubes filled with 500 mg of activated charcoal (20 – 60 mesh, Sigma Aldrich) were used. The charcoal was conditioned by keeping it at  $180 \text{ }^\circ\text{C}$  for 2 h in a nitrogen stream. The sample volume taken at the outlet of the clean-up column amounted to 5 L. The throughput of the sampling pump (Desaga GS 312) was adjusted to 0.5 L/min. Each time, two sampling tubes connected in series were used for sampling and control. Elution of the analyte ethylacetate was done with 10 mL of diethyl ether (p. a., Acros Organics). Measurement was performed with GC/MSD (Agilent 6890/5975C, DB 1301 60 m, 1 mm i.d., 250  $\mu\text{m}$  film, He 1 mL/min). Solvent in the absorber fluid was quantified by means of headspace-GC/MSD (headspace: Agilent Technologies G 1888). Furthermore, continuous measurements of the gas contamination were done with a mobile photo-ionization detector (2020 ComboPro portable measuring instrument, Ansyco).

## 2.3 Gas cleaning experiments with ethylacetate, biodiesel and molecular sieve

150 g conditioned molecular sieve ( $250 \text{ }^\circ\text{C}$ , 2 h) was kept in an aluminum net that was placed in the absorber reservoir in such a way that all the absorber fluid, flowing back from the clean-up column, had to pass through the molecular sieve layer before it was kept in motion by a magnetic stirrer at the bottom of the reservoir.

Gas analysis was done with the photo-ionization detector. In the course of each experiment, the inlet ethylacetate concentration was measured four to six times. Degree of purification, given in [%], was calculated from the inlet and outlet ethylacetate concentrations given in [ $\text{g/m}^3$ ]. For quality control, ethylacetate concentrations were additionally determined by applying charcoal tubes for sampling and GC/MSD for analysis (section 2.2).

## 2.4 Molecular sieve regeneration

Thermogravimetric (TG) measurements were conducted in order to determine the optimum regeneration temperatures of the molecular sieve, loaded with ethylacetate as well as with water (deionized), ethanol (p. a., Riedel-de Haen), and iso-hexane (p. A., Biesterfeld), respectively. The mass ratio of molecular sieve and adsorbed solvent was 10:1. For loading, 30 g of molecular sieve and 10 g of solvent were separately placed in a closed desiccator. Within 24 h, the solvent was completely adsorbed by the molecular sieve.

TG measurements were conducted with TG 209 F1 (Netzsch, Germany). Molecular sieve samples spiked with ethylacetate of an initial weight 0.44 – 0.46 g were heated from  $25 \text{ }^\circ\text{C}$  up to  $1,000 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The samples were placed in  $\text{Al}_2\text{O}_3$ -cups and  $\text{N}_2$  was used as inert flushing gas. Additional TG measurements with the instrument TGA/DSC 1,

Mettler Toledo, allowed the online analysis of emitted gases with mass- and infrared-detectors.

A sufficiently sized facility was erected that allowed to collect condensate during molecular sieve regeneration. In each experiment, 100 g molecular sieve having 10 g solvent adsorbed and charged with 30 g lauric acid methylester (LM) as an individual biodiesel component was kept at 180 °C for 4 h. The experiments were conducted with ethylacetate as well as with ethanol, iso-hexane, and water. For regaining the solvent, a water-cooling and a cryo-trap filled with liquid nitrogen were connected in series. Nitrogen was applied as carrier gas flowing through the molecular sieve layer with a rate of 0.5 L/min. In the water cooler, mostly LM was condensed in small amounts, whereas the solvent vapors were frozen in the cryo-trap.

In a second regeneration step, the molecular sieve was treated at a temperature of 500 °C with synthetic air supply (Westfalen AG) in order to completely remove adsorption residues. For these regeneration experiments, 10 g molecular sieve charged with 1 g ethylacetate and coated with 3 g LM were placed in a glass boat. In a glass tube, surrounded by a ring oven, the samples were first treated at low temperature and subsequently thermolyzed at 500 °C for 2 h in an air stream of 0.5 L/min.

### 2.5 Adsorption isotherms

For the experimental results introduced here, especially the isotherms after Langmuir and Freundlich were of relevance. They were applied as described in the following.

#### *Langmuir isotherm*

This model implies that the binding energy between surface and adsorbate is consistent and that the adsorbate molecules arrange in a monolayer on the adsorbent's surface. This model also premises that there are no interactions between molecules on neighboring positions [20]. The Langmuir isotherm is described by the following equation:

$$q_e = \frac{Q_0 \cdot k_L \cdot C_e}{1 + k_L \cdot C_e}$$

$q_e$ : mass of the adsorbates in relation to the adsorber mass in the state of equilibrium [mg/g];  $C_e$ : concentration of the adsorptive in the liquid or gaseous phase in the state of equilibrium [mg/L];  $Q_0$ : adsorption capacity [mg/g];  $k_L$ : Langmuir constant related to the free adsorption energy [L/mg] [21].

#### *Freundlich isotherm*

For the Freundlich isotherm, the adsorption on a heterogeneous adsorption surface as well as a multilayer adsorption can be described [22]. Different from the Langmuir isotherm, the

Freundlich equation contains no maximum adsorption capacity [23]. The Freundlich isotherm is described by the following equation:

$$q_e = k_f \cdot C_e^{1/n}$$

$q_e$ : mass of the adsorbates in relation to the adsorber mass in the state of equilibrium [mg/g];  $C_e$ : concentration of the adsorptive in the liquid or gaseous phase in the state of equilibrium [mg/L];  $k_f$ : Freundlich adsorption coefficient;  $1/n$ : factor of heterogeneity. The factor of heterogeneity ranges between 0 and 1. The smaller the factor, the more heterogeneous is the adsorber surface [21].

### 2.6 Adsorption isotherms for the combination molecular sieve and ethylacetate

The experiments for the determination of the adsorption isotherms were conducted in a temperature controlled chamber at 25 °C. In each experiment, 30 g of conditioned molecular sieve and a defined amount of ethylacetate were separately placed in a closed desiccator (10.5 L.) The amount of ethylacetate adsorbed on the molecular sieve was determined gravimetrically by measuring its mass increase after 24 h. The initial ethylacetate masses used for the experiments ranged from 2 to 9 g. For the adsorption isotherms, the mass of adsorbed ethylacetate in relation to the adsorber mass was denoted as  $q_e$  [mg/g] and the equilibrium concentration of the ethylacetate in the gas phase  $C_e$  [mg/L] was calculated. The calculation of the adsorption isotherms was done with the curve fitting tool of the MATLAB program package.

### 2.7 Adsorption isotherms for the combination molecular sieve, ethylacetate and LM

Solutions of ethylacetate in LM were prepared in the concentration range of 0.5 to 11 mL/L. Portions of 3 g of molecular sieve were mixed with 40 mL ethylacetate/LM solutions and stirred in an incubator shaker at 50 r/min and 25 °C. When the state of equilibrium was reached after 21 h, the solution was decanted, diluted and analyzed with headspace-GC/MSD (table 1). From the analytical results, the model parameters  $q_e$  and  $C_e$  were calculated (section 2.5). These values were used for the calculation of the adsorption isotherms with the curve fitting tool of the MATLAB program package.

## 3 Results and discussion

### 3.1 Concept overview

The novel concept developed for exhaust air cleaning from solvent vapors is schematically depicted in figure 1. In the exhaust air cleaning unit, gaseous solvents are absorbed in appropriate absorber fluids, working on the countercurrent principle. In order to enhance the cleaning capacity, molecular sieve is additionally placed in the absorber reservoir. It adsorbs the solvent out of the absorber fluid, keeping thereby the solvent concentration in the fluid low and thus increasing the cleaning efficiency for longer periods of time. Once the molecular sieve is completely saturated with solvent, it is regenerated in two steps. First, it is treated at

moderate temperature which allows desorption and recovery of the solvent. Second, it is treated at high temperature in air, aiming at complete regeneration and reuse in the exhaust air cleaning facility.

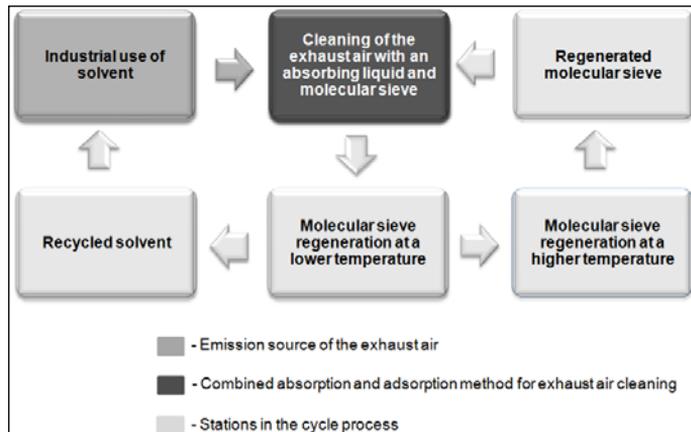


Figure 1: Scheme of the novel exhaust air cleaning process

### 3.2 Exhaust air cleaning experiments with the lab-scale unit

In pilot experiments, different fluids, as for example diethylene glycol dibutyl ether, an ionic liquid, silicone oil, hexadecane, rapeseed oil, biodiesel, and lauric acid methylester (LM) were tested for their ability to act as absorber for the solvents ethylacetate and iso-hexane. The primary selection or elimination criteria were their absorption capacity, release of volatile components, viscosity, compatibility with the molecular sieve, and their price. In general, the solvent absorption capacities of all fluids tested under the defined experimental conditions (section 2.1) were  $\leq 1\%$ , which is not sufficient for technical applications in any case. Nevertheless, biodiesel (source: rapeseed oil) and the chemically better defined biodiesel component LM appeared to serve the purpose at best. Different molecular sieves were tested, as well. Granulates described in section 2.1, were preferred to powder-form molecular sieves because of a better handling, although adsorption capacity of the powders was higher by factor 1.5.

In the following, experimental results are exemplarily introduced that were gained from the combination of biodiesel-absorber, molecular sieve granulate adsorber and ethylacetate as air contaminating solvent (section 2.3). The input concentration of the ethylacetate was regulated to 6.4 g/m<sup>3</sup> which is considered high, from the perspective of industrial practice. From figure 2 it can be seen that the addition of molecular sieve to the biodiesel-absorber resulted in a distinctly better clean-up of the gas that amounted to about 85%. An important positive result of these investigations was that the molecular sieve located within the biodiesel was able to selectively adsorb ethylacetate as well as other solvents like iso-hexane and ethanol (not depicted). One observation was that the gas cleaning immediately after nightly stops, after 7,

17 and 25 hours, was slightly better than before (figure 2). This can be explained by an additional ethylacetate concentration drop in the absorber because of ongoing molecular sieve adsorption.

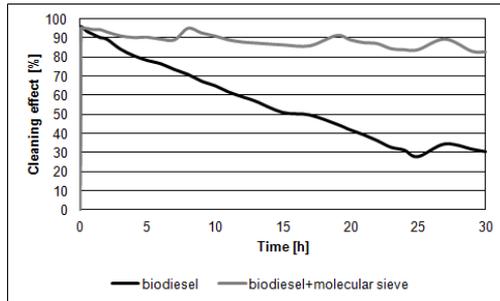


Figure 2: Removal of ethylacetate from artificial exhaust gas by biodiesel and biodiesel plus molecular sieve

Further experiments were conducted in order to test whether the good cleaning capacity was also achieved with a practice orientated low ethylacetate concentration of  $0.8 \text{ g/m}^3$  (section 2.1). The total length of the experiments was 60 h. The results together with those of higher ethylacetate concentration are shown in figure 3. The clean-up rate was comparably lower for a low ethylacetate input concentration at the beginning of the experiments. After 20 to 25 h the rates were equalized and after 40 h and longer, the clean-up in the experiment with low solvent input concentration was even more efficient than in that with high ethylacetate input.

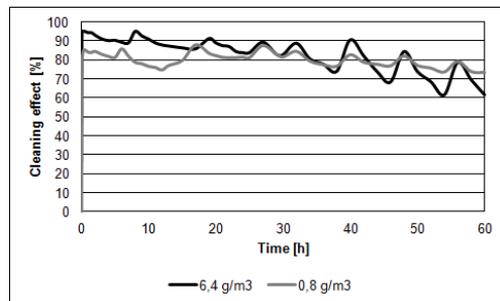


Figure 3: Removal of ethylacetate from artificial exhaust gas by biodiesel or biodiesel plus molecular sieve with different input concentrations adjusted

As can be seen from figure 4, the solvent concentration in the biodiesel slowly increased in the experiment with an ethylacetate input of  $6.4 \text{ g/m}^3$ , indicating a saturation of the molecular sieve with the solvent. In contrast, the solvent concentration remained constant during the 60 h experiment with low ethylacetate input because the molecular sieve did not get saturated in this case. The results of the exhaust air cleaning experiments were compared with the limit value of  $75 \text{ mg C/m}^3$ , given by the German Technical Guideline for Air Pollution Control. As can

be seen in the figure 4, it was successfully achieved that the output concentration was kept below the limit value for the 60 h duration of the experiment in case of an input ethylacetate concentration of 0.8 g/m<sup>3</sup> or 349 mg C/m<sup>3</sup>.

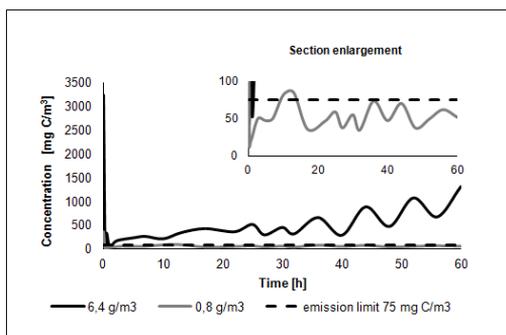


Figure 4: Carbon concentration after cleaning of ethylacetate-contaminated exhaust gas with biodiesel plus molecular sieve

### 3.3 Thermogravimetric measurements for investigating the molecular sieve regeneration

First, differential thermogravimetric measurements were performed with molecular sieve samples charged with ethylacetate. From the curve progressions, three temperature ranges where mass losses are distinctive; these are 160 – 200 °C, 280 – 300 °C and 400 – 540 °C. This temperature specific desorption of the molecules indicates different binding strengths between ethylacetate and the molecular sieve.

After FTIR-measurements for characterizing the gases released during heating revealed that ethylacetate was emitted at the first mass loss maximum (160 – 200 °C). At the second maximum (280-300 °C) the decomposition products ethylene and acetic acid were formed, as well, and in the temperature range 400 – 540 °C methane was additionally found. Methane is one of the decomposition products of ethylacetate which is formed in a temperature range of 1,025-1,525 °C [24], if no active catalytic surface is present. Presumably, the strongly bound ethylacetate was decomposed under the catalytic effect of the molecular sieve and thus removed from its surface.

### 3.4 Molecular sieve regeneration

Orientated at the DTG-measurements as well as single differential thermal analyses (not shown here), regeneration experiments at 180 °C were performed as described in section 2.4.2 with ethylacetate loaded molecular sieve, coated with LM for some of the experiments. For comparison purposes, these experiments were repeated with the solvents iso-hexane, ethanol, and water. Tests revealed an optimum regeneration time of 4 h. Condensates of the trapped solvent vapors were quantified and analyzed for impurities by GC/MSD (for ethylacetate, ethanol and iso-hexane), and Karl Fischer-titration (for water), and the degree of regeneration was calculated based on this. The results are presented in table 2.

Table 2: Loaded molecular sieve regeneration at 180 °C with and without LM addition

	Water	Ethanol	Ethylacetate	Iso-Hexane
Regeneration without LM, solvent recovery [%]	19.9 ± 3.4	5.4 ± 0.8	0.8 ± 0.4	54.3 ± 5.3
Regeneration with LM, solvent recovery [%]	30.4 ± 0.6	76.5 ± 2.5	52.6 ± 1.8	73.2 ± 0.9
Increase factor of solvent recovery	1.5	14.2	65.8	1.3

LM: lauric acid methylester

It was an unexpected positive result that the LM-addition effected an enhanced recovery for all solvents tested (table 2). Under these conditions, the improvement was found to be highest for ethylacetate with an increase factor of solvent recovery of about 66. A direct recycling of the molecular sieve treated at 180 °C for exhaust gas cleaning resulted in adsorption capacities for ethylacetate in the range of 20 to 30%, compared with unused molecular sieve. This finding led to the necessity of the implementation of a second regeneration step (figure 1). The solution to this problem was, to keep the molecular sieve additionally at 500 °C in air for 2 h (section 3.3), in order to destroy and remove remaining substances by complete oxidation (section 2.4.3). Afterwards, the adsorption capacity of the molecular sieve remained the same as that of unused sieve, even when used and recycled three times.

### 3.5 Adsorption isotherms

Outcomes of adsorption experiments were set in reference to various isotherms after Langmuir, Freundlich, Redlich-Peterson and Sips, whereas the first two proved to be relevant for the systems investigated here. The results are given in table 3.

Table 3: Parameters of the Langmuir and Freundlich adsorption isotherms for ethylacetate adsorption from the gas phase and out of solution

Model	Parameter	Adsorption isotherms medium air	Adsorption isotherms medium LM
Langmuir	$Q_0$	230.3	81.3
	$k_L$	0.3015	0.0269
	$R^2$	0.9628	0.9283
Freundlich	$k_F$	106.9	15.3
	$n$	6.431	3.997
	$R^2$	0.8319	0.9675

$Q_0$ : adsorption capacity [mg/g];  $k_L$ : Langmuir constant related to the free adsorption energy [L/mg];  $k_F$ : Freundlich adsorption coefficient;  $n$ : strength of adsorption;  $R^2$ : correlation coefficient

## 4 Conclusions

A combined absorption and adsorption procedure for air cleaning was developed and investigated and it was successfully applied in laboratory-scale essentially to the combination ethylacetate as air polluting solvent, biodiesel as absorber fluid and a molecular sieve as adsorbent. A continuous cleaning of the absorber fluid from the solvent was achieved by the added molecular sieve. The complete regeneration of the molecular sieve could be realized. It was demonstrated that this process was in principle also applicable to other air polluting solvents. Due to the combination of a liquid organic absorber with a solid adsorber, it is possible to adapt the system to highly polluted exhaust air as well as to high exhaust air flow rates.

## 5 Acknowledgment

We express our sincere thanks to the Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V. (AiF) for funding this project concerning exhaust air cleaning.

## 6 References

- [1] N. Ebeling, Abluft und Abgas. Reinigung und Überwachung, Wiley, Weinheim 1999, p. 233.
- [2] Umweltbundesamt, Nationale Trendtabellen für die deutsche Berichterstattung atmosphärischer Emissionen (2011); [www.umweltbundesamt.de/emissionen/publikationen.html](http://www.umweltbundesamt.de/emissionen/publikationen.html)
- [3] S. Kalmbach, Technische Anleitung zur Reinhaltung der Luft – TA Luft, Erich Schmidt Verlag, Berlin 2004, p. 475.
- [4] K. Ohlrogge, J. Wind, Membranverfahren in der Abluftreinigung, VDI Berichte Nr. 1722, VDI Verlag, Düsseldorf 2002, p. 69-80.
- [5] E. Moretti, Reduce VOC and HAP Emissions, Chem. Eng. Progr. 2002, 6, 30-40.
- [6] J. Berty, Quasi steady-state method of catalyst evaluation for air pollution control, Environ. Prog. 2007, 26/1, 43-49.
- [7] F. Heymes, P. Demoustier, P. Moulin, F. Charbit, J. Fanlo, VOC removal from gaseous emissions by a hybrid process: absorption und pervaporation, Chem. Eng. Sci. 2007, 62, 2576-2589.
- ..... etc.
- ..... etc.
- [23] B. Volesky, Sorption and biosorption, BV Sorbex, Inc. 2003, Montreal – St. Lambert, p. 316.
- [24] K. Saito, T. Sasaki, I. Yoshinobu, A. Imamura, Thermal decomposition of ethylacetate. Branching ratio of the competing paths in the pyrolysis of the produced acetic acid, Chem. Phys. Lett. 1990, 170, 385-388.