Project Report

Characterization and Modification of SIEMENS gas analyzer FIDMAT 6 to achieve certification for emission monitoring according to DIN EN 15267-3 (2008).

Reutlingen, 17 July 2017

Submitted by:

Dorian Lukas Segadlo (PATM3)

Mahmood Mubarak Rajput (PATM3)

Table of Contents

Acknowledgement

This POL-Project was carried out at the Process Analysis and Technology Centre (PAT) and also the Reutlingen Research Institute (RRi) of the Reutlingen University from April 2017 until July 2017.

We would like to thank Prof. Dr. Karsten Rebner for giving us opportunity to work on this project. We are highly thankful to Tobias Drieschner, MSc. for his great supervision throughout our project work and we would also like to mention many thanks to Mona Stefanakis, MSc. for supervising us in initial phase of project. We are again thankful to both of them for all the helpful meetings, phone calls and discussions.

In addition our gratitude goes to our cooperation company SIEMENS AG, Karlsruhe, especially to Mr. Andreas Sutter who was our contact persons in this project. We are also thankful to Mr. Josef Richter and Mr. Ricardo Calvo for presenting to us their laboratory setup and answering our questions regarding the project. We are thankful to all of them for their competent advice, support and the invitation to their company.

And of course we would like to mention special thanks to Prof. Waltraud Kessler for her great help concerning questions about design of experiment.

List of Tables:

List of Figures:

1 Introduction

1.1 Motivation

Volatile organic compounds (VOCs) are a large group of organic chemicals that include any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate). VOCs are of interest in part because they participate in atmospheric photochemical reactions that contribute to ozone formation[1]. The high concentration of VOCs in environment are causing various serious health issues i.e. eye, nose, and throat irritation; headaches, loss of coordination, nausea; and damage to the liver, kidney, and central nervous system and in some cases cause cancer [2]. Therefor the control of VOCs emission to environment accounts for integral part of the government's environmental protection policies.

The air pollution control has been a serious concern in environmental policies of European Union (EU) since the late 1970s. The Directive 2016/2284/EU of the Clean Air Policy Package (2020-2030) for EU set goals for reduction of emissions on national level for certain atmospheric pollutants. The pollutants with their reduction targets for 2030 include Sulphur dioxide (-79%), nitrogen oxides (-63%), volatile organic compounds (-40%), ammonia (-19%) and fine particulate matter (-49%) which are responsible for acidification, eutrophication and ground-level ozone pollution, leading to significant negative impacts on human health and the environment[3].

There are various sources of VOC emission, including motor vehicles, chemical manufacturing facilities, refineries, factories, consumer and commercial products, and natural (biogenic) sources (mainly trees)[1]. On industrial scale stationary large combustion plants, gas turbines, incinerators, and cement plants account for the largest proportions of overall hydrocarbon emission in atmosphere. In order to comply with regulatory authority standards for industrial emission, the operators of industrial plants must monitor these emissions. The systems which continuously measure stack-emissions are known as Automated Measuring Systems (AMSs) or Continuous Emission Monitoring Systems (CEMSs). CEMSs for hydrocarbon measurement uses different sensor technologies, including: catalytic; photo-ionization; infra-red; gas chromatography; and flame ionization detection (FID)[4]. FID is considered to be the most accurate and the most reliable method to measure VOCs in stack gases.

There are many companies providing CEMSs solutions for various gases. SIEMENS AG is one of the renowned solution providers in the field of continuous gas analysers. It produces a series of analyzers which are extremely accurate, reliable and efficient in continuous gas analysis, for chemical and hydrocarbon customers[5]. These devices make their process economical and reliable at various process stages. FIDMAT 6, SIEMENS gas analyzer, based on FID techniques, offers a reliable mean for continuous monitoring of VOCs in stack emission and the goal of this project is to work in collaboration with the SIEMENS to further optimize the performance of FIDMAT 6 analyzer.

1.2 Objective

The POL project has been divided in to two major parts and each part has sub objects as explained in following section:

FIDMAT 6 SIEMENS gas analyzer:

- Analysis of performance characteristics of FIDMAT 6, as defined in project document i.e. response factor and cross sensitivity.
- Evaluation of experimental data provided by SIEMENS based on DoE proposed by M.Fajar[6] using RSM.
- In case of unsatisfactory results new parameters will be investigated and new DoE will be purposed.

ABB AO2000-Fidas24 gas analyzer:

- Installation, commissioning and safe operation of Fidas24 Gas Analyzer at Process Analytical Laboratory.
- Define safety protocol for safe operation of gas analyzer.
- Define standard operating procedure for Fidas24 Gas Analyzer so that in future further reproducible experiments can be performed with the device.
- Performance of test experiment by testing carbon content of some organic gas mixtures using gas mixing device.
- Finally the device will be used as reference device for FIDMAT 6, and parallel experiments will be performed so that FIDMAT 6 can be optimized.

2 Literature Review

2.1 FID Technology

The flame ionization detector (FID) was first introduced in Newzeland in 1958. Since then it's been used as sensitive quantitative monitor of organic compounds in gas chromatography and for monitoring mixtures of hydrocarbons[7]. There are several reasons for the success of FID technology. It has very low noise level, linear response over very wide range, high sensitivity to hydrocarbons and its optimized response varies very little with factors such as detector temperature, flow rates of hydrogen, carrier gas and other parameters. The following sections will discuss the working principle and technical aspects of FID method for determination of VOCs in gases.

2.1.1 Working Principle of FID

The working principle of the FID is based on the ionization of unburned hydrocarbons in the hydrogen flame. The ionization current measured by the FID depends on the number of carbon atoms present in hydrocarbon. Its output may be displayed in one of the two ways as ppm of hydrocarbon or as milligrams of carbon per cubic meter (mgC/m3). There are different configurations of flame ionization detectors, Figure 1 illustrates the principle of FID.

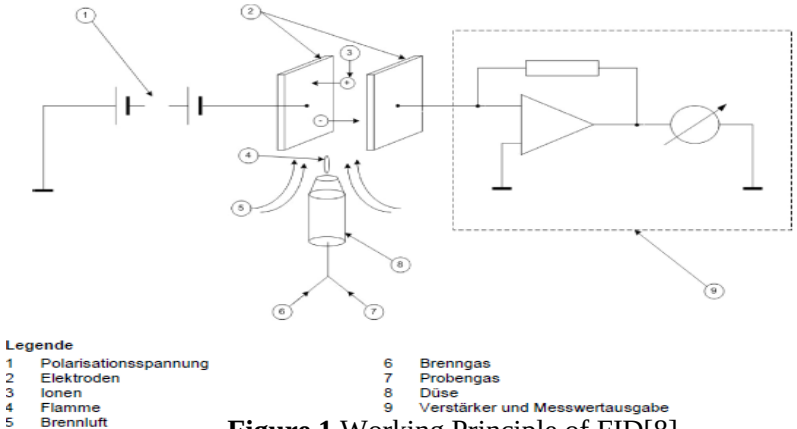

Figure 1 Working Principle of FID[8]

When the proper ratio of hydrogen to air is established in the combustion chamber, the flame is ignited with a glow plug. The sample gas is then passed through the flame, the combustible organic compounds in the flame will be ionized and passed through an electric field. The ionized

hydrocarbon will generate a small current which is proportional to the number of carbon atoms present in the molecule. An amplifier is then used to amplify the detector current[9].

The main advantage of FID is that it measures only organically bound carbon present, and is therefore non-sensitive to gases like argon, carbon dioxide, nitrogen, water vapor, etc.) which are not ionized by the FID, and thus are not measured[10].

2.1.2 Factors Influencing FID Measurements

The technical standard DIN EN 12619 highlights the various parameters which influence the FID measurements even if the concentration of the hydrocarbons in the sample gas is constant. These parameters are as following:

2.1.2.1 Sample Gas Flow

The sample gas volume flow has the proportional influence on the FID signal. When the volume flow of sample gas is increased, more ions are present between the electrodes and the current becomes stronger.

The mixture of the sample gas and the fuel gas is usually adjusted by critical nozzle position, which must be clean. The contamination of the nozzle will result in reduction of current measured by FID [11]. In order to prevent the contamination of the FID, the sample gas is filtered before it enters the device and also to avoid the condensation of vapours in the device, the sample gas is heated before it enter the combustion chamber. The sample gas flow may also be influenced if the particle filter is clogged which will result in lower output of the device[12].

2.1.2.2 Combustion Chamber

If the sample gas carries the silicon-containing compounds, the electrodes will gradually be coated with silicon oxides which is strong electrical insulator. This will reduce the current caused by the combusted gas and the measured value becomes lower, which results in lower signals[13].

2.1.2.3 Combustion Air

The combustion air should be free from any hydrocarbons or at least fulfil the air quality standards. The presence of hydrocarbon in combustion gas will result in higher ion current which will cause

error in measurements. To circumvent this problem, synthetic combustion air consisting of N_2 with a proportion of 20.9% O_2 is often used.

2.1.2.4 Cross-Sensitivity

Cross sensitivities are caused by components in the sample gas, which influence the FID measured value, without the concentration of the hydrocarbons in the sample gas changing.

Typical components with cross-sensitivity are gases such as SO_2, NO, NO_2. Cross sensitivities can cause both positive and negative deviations. Cross sensitivities are not necessarily linear. They also depend to a certain extent on the design of the device[8].

2.1.2.5 Oxygen Influence

Oxygen also causes cross-sensitivity. The higher the oxygen content in the sample gas-fuel gas mixture, the shorter is the period during which the hydrocarbons are ionized prior to their oxidation, and the measured values become lower, resulting in an under-estimation of the concentration[14]. The transverse sensitivity to oxygen can be reduced by constructive measures on the device, but also depends on the different volume flows and the composition of the test gases.

2.1.2.6 Response Factors of Gases

The ion current in the FID flame is proportional to the number of carbon atoms in the gas under investigation over a large range. However, the molecular structure (single or double bond, number and type of heteroatoms, chain length and ring structures) has a considerable influence on the oxidation behaviour of the carbon atoms and therefore on the strength of the detector signal[15]. Organic compounds with oxygen as heteroatom are generally indicated with significantly lower sensitivity than pure hydrocarbons with the same number of carbon atoms per molecule. Thus, their response factors are lower than those of the pure hydrocarbon compounds.

2.1.3 Responses Factor of Different Compounds

A Flame Ionization Detector (FID) is basically a carbon ion counting device. Its response is directly proportional to the number of carbon atoms present in sample being analysed. It measures the carbon content of the VOC in mgC/m^3. However the response is affected by a number of factors as physical detector cell design limitations, the physics of the ion stream in the hydrogen

flame and most importantly molecular structure and composition of the gas[11]. Therefore FID output usually is not equal to the actual carbon count. FID are normally calibrated with propane span gas whose response factor is set to 1. The actual carbon content of a hydrocarbon can be calculated in mgC/m^3 from the measures value if the response factor is known. The response factor is calculated as following:

$$f_c = \frac{\frac{S_i}{C_{c,i}}}{\frac{S_{ref}}{C_{c,ref}}} \quad (1)$$

f_c = Response factor related to carbon;

S_i = FID (measurement signal) for the substance i;

S_{ref} = FID (measuring signal) for propane;

Cc, i is the carbon concentration of the substance i, in mg / m^3 (273 K, 101.3 kPa);

Cc, ref is the carbon concentration of propane, in mg / m^3 (273 K, 101.3 kPa).

Table 1 Response factor performance criteria for CEMS measuring TOC for laboratory testing[16]

Performance characteristic	Performance criteria
Effect of oxygen	≤ 2 % A
Range of response factors:	
Methane	0.9 to 1.2
Aliphatic hydrocarbons	0.90 to 1.10
Aromatic hydrocarbons	0.8 to 1.1
Dichloromethane	0.75 to 1.15
Aliphatic alcohols	0.7 to 1.0
Esters and ketones	0.7 to 1.0
Organic acids	0.5 to 1.0
A:Percentage value as percentage of the upper limit of the certification range.	

2.1.4 Cross Sensitivity

The technical standard DIN EN 15267-3 specifies the performance characteristics of FID analysers to determine TOCs in stack gases. Cross sensitivity is one of the main performance characteristic that manufactures must fulfil. It is defined as response of the FIDs to compounds other than those that it is designed to measure.

The standard also specify the interferent and their concentrations which are listed in Table. Cross sensitivity test are normally done by first introducing the Test gas without interferent and then with the interferent. The measured signals of the FID shall be determined for each test gas by waiting the time equivalent to one independent reading and then recording three consecutive individual readings. The three individual readings shall be averaged. The deviations between the average reading with and the average reading without the interferent present at the zero point and span point shall be determined for each interferent.

Table 2 Concentrations of interferents used during cross sensitivity tests[16]

Interferent	Concentration or volume concentration	
	Value	Unit
O_2	3 A and 21	%
H_2O	30	%
CO	300	mg/m^3
CO_2	15	%
CH_4	50	mg/m^3
N_2O	20	mg/m^3
N_2O (fluidised-bed firing)	100	mg/m^3
NO	300	mg/m^3
NO_2	30	mg/m^3
NH_3	20	mg/m^3
SO_2	200	mg/m^3
SO_2 (coal-fired power stations without desulphurisation)	1000	mg/m^3
HCI	50	mg/m^3
HCI (coal-fired power stations)	200	mg/m^3

In the above section, basis working principle and the factors affecting the measurement results of FID are discussed in detail. As FID is a carbon counting device that measures carbon in volatile gases in terms of mgC/m^3 but in actual practice FID output is not equal to the actual carbon count due to detector cell design limitations, the physics of the ion stream in the hydrogen flame and most importantly molecular structure and composition of the gas. During the course of this project the knowledge of these influencing factors will be quit helpful in order to select right factors and their ranges for robust DoE.

3 Material and Method

3.1 Experimental Setup for Siemens FIDMAT 6 Gas Analyser

The experimental setup for preliminary measurements was established at SIEMENS laboratory in Karlsruhe where all the proposed experiments where performed by SIEMENS' team. Due to company privacy policy it was not possible to take any picture of their laboratory setup or disclose any information regarding their setup and also it is not in the scope of this project. The gas flow diagram in figure 2 has been helpful to understand laboratory settings. the The following section deals with the materials (sample gases) used in preliminary phase, FIDMAT 6 gas analyser and the Design expert software used for data analysis.

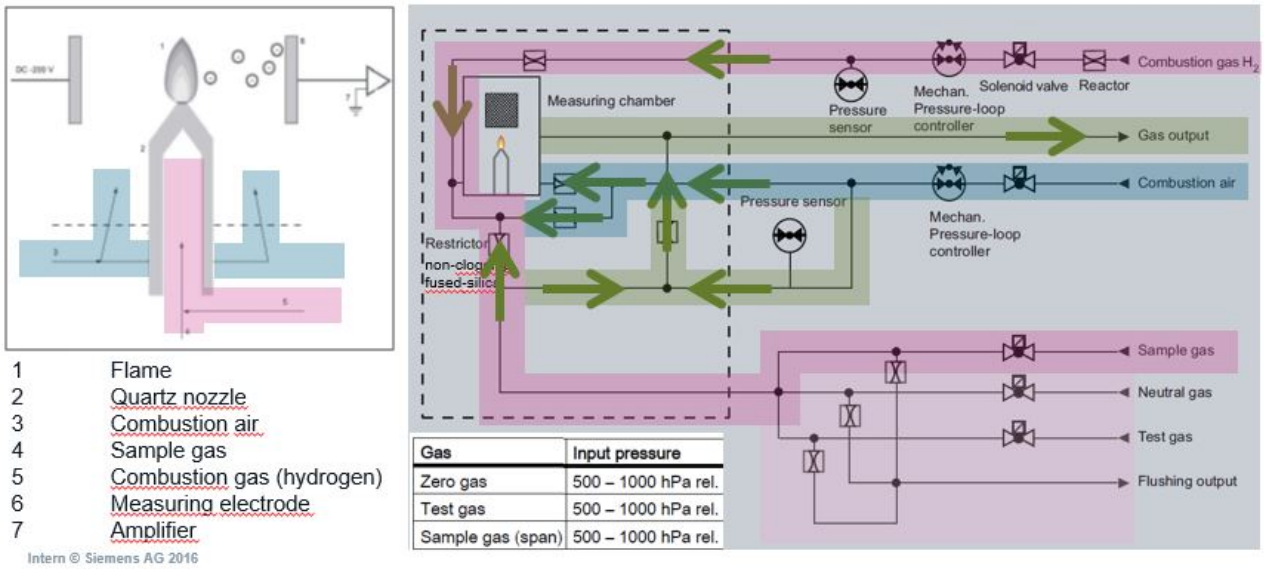

Figure 2 A schematic drawing of the experimental set up.[17]

3.1.1 Sample Gases

The DIN EN 12619 standard specify the performance criteria including response factors for TOC analyser based on flame ionisation detection (FID) method, for different Hydrocarbon groups as listed in Table 1. In the initial phase of the project, 8 sample gases (Propane, Toluene, n-Butanol, Ethyl acetate, Benzene, n-Octane, Dichloromethane, and Methanol) were selected and their response factor were determined at instrument setting proposed in DoE.

3.1.2 FIDMAT 6

FIDAMAT 6 is an extractive gas analyzer that is designed to measures consistently the total hydrocarbon. It is based on the FID measuring principle. Gas analyzers with a FID from SIEMENS are well suited for the continuous total hydrocarbon measurement. The FIDAMAT versions cover a broad scale of utilizations that is capable of measuring hydrocarbons (TOC) in pure and ultra-pure gases.

It is also important to fulfil the requirement for the purity of the zero gas, test gas and operating gases before starting any measurement. The detection limit of the device lies at approx. 30 ppb [18]. As compared to other comparable devices, the FIDAMAT 6 has distinct built in features as following[17]:

- It has a very low sensitivity to cross-gases.
- A low consumption of combustion air.
- Its response factors are very little influenced from oxygen.

Certain interest has been paid to the safety functions after an automatic start following the warm-up condition together with automatic measuring system and self-diagnostic. In case of accidental extinguishing of the detector flame, it is automatically re-ignited. The reference 17 covers the detailed description of FIDMAT 6 gas analyzer. As far as its applications are concerned it is one of best widely used device to monitor TOC in exhaust gases in chemical plants, gas manufactures (ultra-pure gas monitoring), re-search and development, cement industry (measurements of emissions), paint shops and dry-cleaning systems, refineries (tank farms, wastewater), drying systems, solvent recovery systems and pharmaceutical industry [19].

3.1.3 Design of Experiment

The Design Expert software is a powerful software tool for both exploring new processes and achieving advanced knowledge of current processes that leads to the optimization of these processes in order to achieve best performance. The software provides highly efficient Design of Experiments for Factorial Designs, Response Surface Methadology, Mixture Design techniques and combined designs. In order to successfully work with Design Expert Software, it is important

to clearly define the objectives of experimentation, responses to be analysed, factors to study and their levels, sufficient number of runs that provide enough power to estimate the effects, replicate runs, centre points and blocks.

In regards to the performance analysis of extractive SIEMENS gas analyzer FIDAMAT 6, the application of response surface methodology (RSM) in optimizing the important factors would be the best choice. It is broadly applied in statistical tools for process optimization in many scientific fields [20]. As a multivariate technique, RSM uses a combination of mathematical and statistical tools to define how various factors impact responses on a data set. This method permits the fitting of a polynomial equation to experimental data. It also enables the extrapolation of a mathematical model to present predictions and identify which factors, and their potential interactions, may influence the various experimental responses. Moreover, the main objective in this method is to optimize the response surface that is affected by different process parameters.

3.1.3.1 Selection of Factors and Response for DoE

In the preliminary stage of the project the four important factors and their ranges for the DoE where finalized after the detailed discussion with the SIEMENS team as shown in Table 3. Also in the initial phase in order to confirm the suitability of factor ranges 8 gases where selected as (Propane, Toluene, n-Butanol, Methyl acetate, Benzene, n-Octane, Dichloromethane, and Methanol). The response factors of the selected gases where then used as response values for DoE analysis.

H_2	Air Premixing	Air Rewind	Tensile Stress
8 – 10 mL/min.	0 – 10 mL/min.	250 – 500 mL/min.	200 and 220 Volt
12 - 16 mL/min.	0 – 20 mL/min.	250 – 500 mL/min.	
17 – 25 mL/min.	0 – 25 mL/min.	250 – 500 mL/min.	

Table 3 Measurement ranges for the DoE.

3.2 Experimental Setup for ABB Fidas24 Gas Analyser

3.2.1 Advance Optima AO2020 Fidas24

The market research study focusing on the companies that manufacture gas analyzer based on FID measuring principle, shows that their analyzers were also tested and certified according to the European standard DIN EN 15267-1 (2009), DIN EN 15267-2 (2009), DIN EN 15267-3 (2008) and DIN EN 14181 (2015) approved by TÜV Rheinland Energy GmbH, a certification body. The study results show that only the company SICK AG and ABB Automation GmbH have fulfilled the requirements for the regulation of DIN EN 15267–3 for continuous emission monitoring system. [6].

The AO2000-Fidas24 is an extractive gas analyzer, which is designed for continuous measurement of the concentration of individual components in gases or vapors. The AO2000 series analyser features include self-monitoring, fault detection, logging and messaging functions. The device consist of two major parts as Analyzer module and Electronic Module. The sensing element and the pneumatic system to monitor and control gas flow are housed in Analyzer Module. The electronics module incorporates the system controller with the I/O modules. The system controller performs the signal processing functions and also communicates with the other functional units of the gas analyzer (e.g. the analyzer modules) via the system bus. I/O module provides interface for controlling the parameters of analyzer module. The Fidas24 gas analyzer has following working ranges, as 0 - 15 mgC/m^3, 0 – 50 mg/Cm^3, 0 – 150 mg/m^3 and 0 – 500 mg/m^3 for supplementary measurement ranges. This device is approved at ambient temperature range of +5°C to +45°C[21].

3.2.2 Installation Guide

In this section the plan for installation work of Fidas24 gas analyzer is discussed. In the beginning of project it was decided that analyzer will be installed in the PAT Laboratory and the VOC of gas mixtures will be determined. For that purpose working packages 6 and 7 were designed. But due to delays in supply of components and shifting of analyzer to SIEMENS laboratory these working couldn’t be achieved completely. The analyzer was provided with operational manual in which all

installation and commissioning work details were available and therefore using the manual installation work was planned in to the following steps:

1. Preparation of safety information for working with Analyzer. It is discussed in detail in section 9 of this report.
2. Preparation for the installation of gas analyzer:
   This task includes the identification of suitable place for gas analyzer in PAT laboratory. It also includes the purchase of gas fitting for making gas connection. In this regard Swagelok was consulted to find out the most suitable gas connection fitting.
3. Once the gas fitting are available the gas lines can be connected to analyzer module by following the guidelines mentioned in operational manual.
4. In order to make electrical connection, electrical leads were supplied with analyzer, the operational manual also give the guideline for this step.
5. When all the installation work is completed its necessary to verify that nothing is left by following a check list mentioned in the manual.
6. Before we start measurement it's also important to purge the gas paths and housing. Also manual guidelines should be followed.
7. At this point analyzer will be ready to measure the VOC in sample gases.

3.2.3 Laboratory Setup

In this section the element of proposed laboratory setup for installation of Fidas24 analyser are shortly discussed. As discussed in the above sections the gas analyser consists of two major modules. All the gas connections are made at analyser module. For normal operation of analyser four inlet gas connections are required as: Combustion gas (H_2), Combustion Air (ambient air), and Instrument Air (N_2) and propane gas as calibration gas. For sample gas a gas mixing device from Burkert is proposed. It has two outlet and four inlet port. One inlet port will be connected to propane gas supply line and the remaining other three port can be connected to desired sample gases. This gas mixing device has touch screen display where output of sample gas flow rate and proportion of each sample gas can be precisely adjusted. The flow controller ranges of gas mixing device are: 0-10 SCCM (lowest range); 0-50 SLM (highest range).

It is also important to note that in order to avoid errors in measurement the quality of all gases should be as per defined in manual. The flow restrictor was suggested only for combustion gas supply line because of safety reasons. The flow restrictor will restrict the flow of H_2 to a maximum of 10 L/hr. In the analyser module there is also one outlet for exhaust gases.

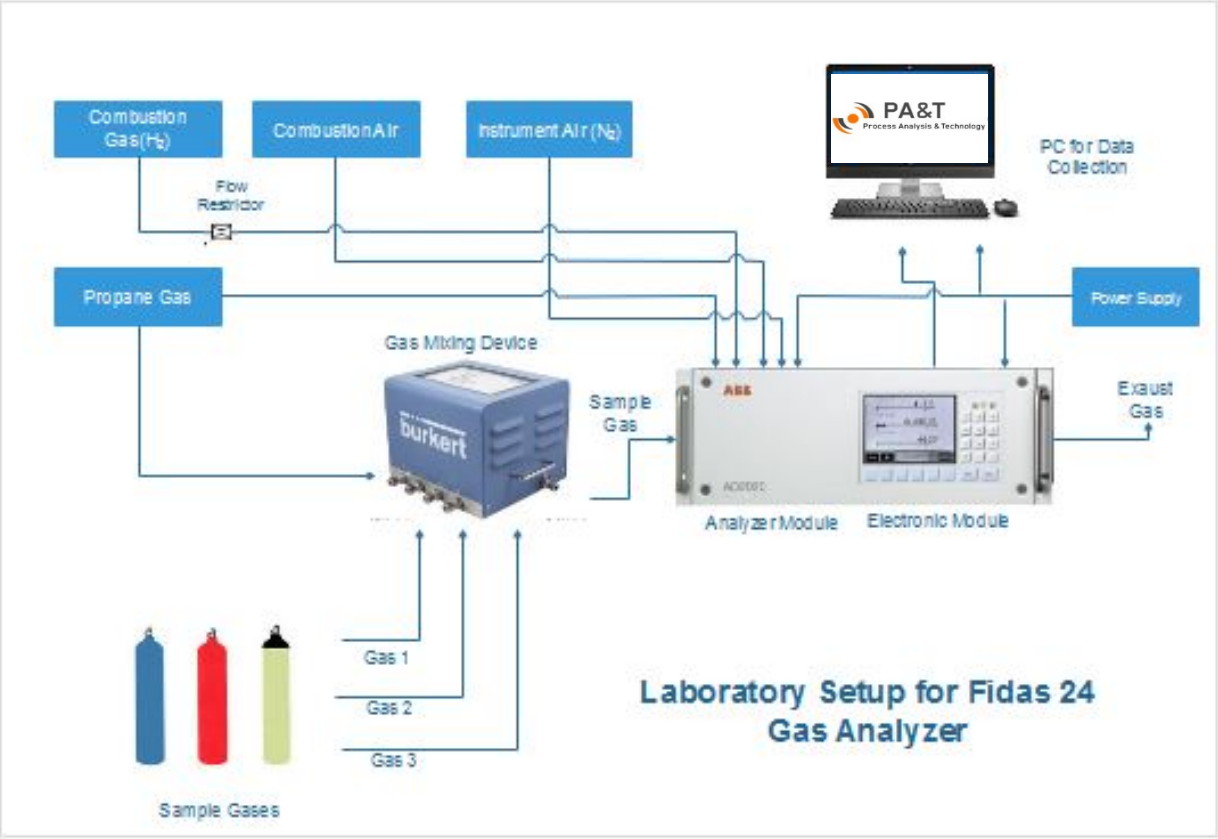

Figure 3 Schematic for Laboratory setup.

The data can be collect through electronic module either by connecting it to Analog to digital converter using I/O ports or it can be connect to a Desktop computer using Ethernet cables. Both modules require separate power supply.

4 Results and Discussion

4.1 Performing DoE in Initial Stage

The proposed DoE has to be perform on two parallel FIDMAT 6 devices to make results statistically significant. In the initially proposed DoE there where 36 experiment for each device (as shown in table A.1 in Appendix A), while conducting experimental runs it was observed that 4 runs out of 18 runs where not possible to perform. The reason was the flame goes off at those parameters. In figure 4, a simple graph column representation is used to highlight this issue, a diagonal is drawn through a region above no experiment could be performed due to flame lost. Therefore those 4 runs where deleted from the initial design space because we had no response values for these runs.

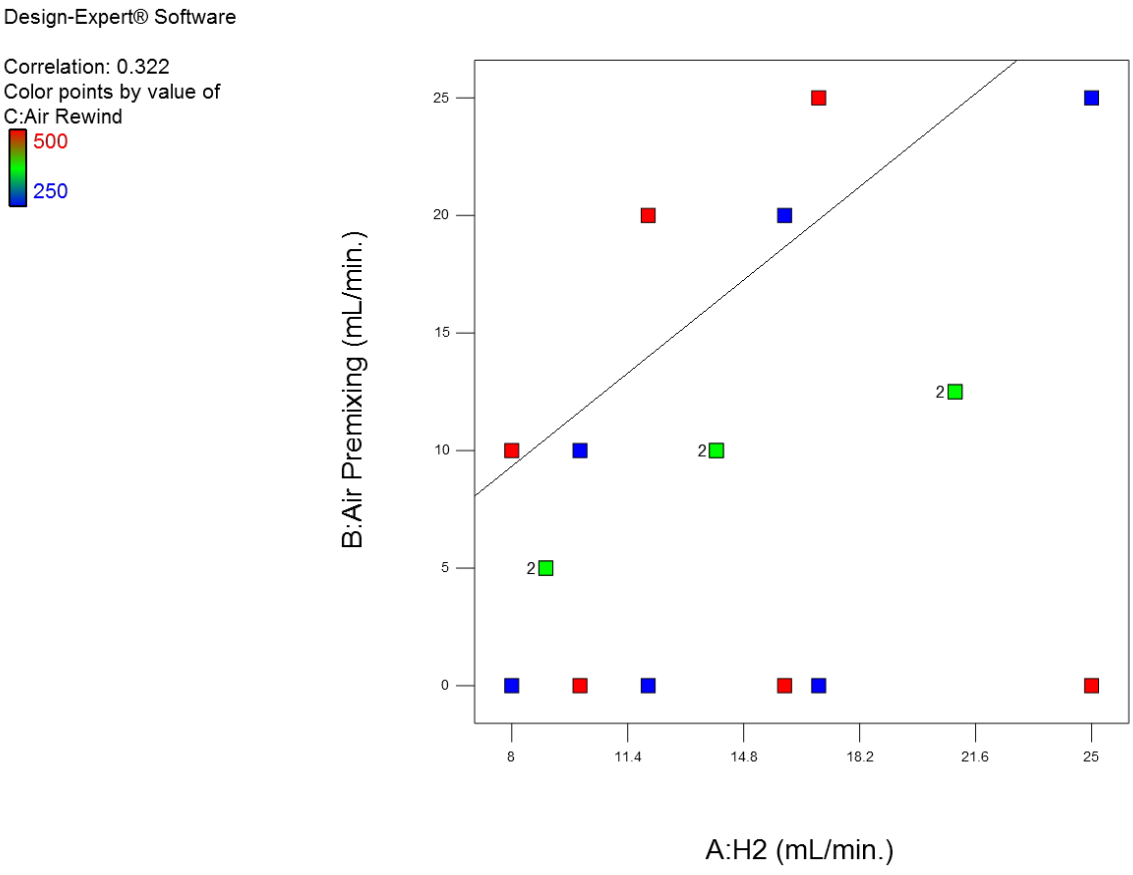

Figure 4 Graph column for 18 experimental runs with tensile stress of 200 V.

4.2 Final Design Space

The graph column in figure C represents the final design space with 14 runs for which we had response values and only these 14 experimental runs where used in the analysis.

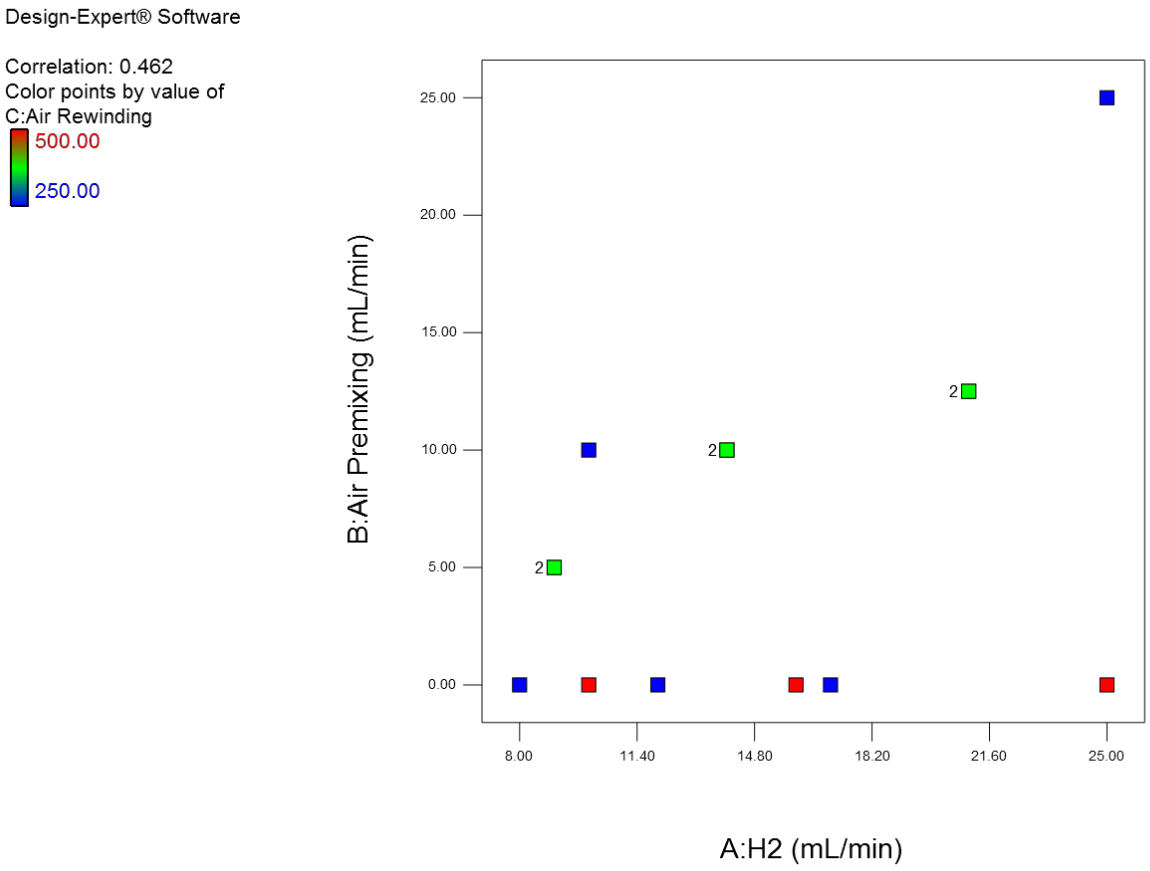

Figure 5 Graph column for 14 experimental runs with tensile stress of 200V.

In order to keep experimentation simple, SIEMENSE separated the 36 runs for single device according to voltage settings. In this way there will be 18 experiments for each voltage setting to be analysed as shown in Table 4. Till now in this project only first set of experiments with device 1 and voltage setting at 200 V were performed and were then analyzed.

In this table, the second row indicates the allowable measuring response factor ranges of each gas according to DIN EN 15267-3 (2008) standardization. It is interesting to note that the response values of only two gases i.e. propane and methanol are in specified range for all runs, in contrast to

it experimental values for n-Butanol and Methyl Acetate, highlighted in red colour, are far below the minimum value of response range.

The response values for other four gases like Toluene, Benzene, Octane and Dichloromethane were found to be fluctuating around the maximum or minimum of specified range. However in order to extract the optimal operating ranges for factors such that maximum response values lie with in specified range Design Expert software was used to analyse the data. The detailed description of analysis is explained in next section.

Run	Device	Factor 1 A: H_2 mL/min.	Factor 2 B: Air Premixing mL/min.	Factor 3 C: Air Rewind mL/min.	Factor 4 D: Tensile Stress V	Response 1 **Propane** mL/min.	Response 2 **Toluene** mL/min.	Response 3 **n-Butanol** mL/min.	Response 4 **Methyl Acetate** mL/min.	Response 5 **Benzene** mL/min.	Response 6 **Octane** mL/min.	Response 7 **Dichloromethane** mL/min.	Response 8 **Methanol** mL/min.
Response Factor Ranges -->						**1**	**0,80 - 1,10**	**0,90 - 1,10**	**0,70 - 1,00**	**0,80 - 1,10**	**0,90 - 1,10**	**0,75 - 1,15**	**0,70 - 1,00**
1	1	8	0	250	200	1.00	1.10	0.59	0.54	1.08	1.15	0.88	0.77
2	1	10	10	250	200	1.00	1.27	0.56	0.63	1.40	1.08	1.67	0.82
3	1	10	0	500	200	1.00	1.10	0.59	0.54	1.07	1.13	0.89	0.77
4	1	14	10	375	200	1.00	1.20	0.57	0.60	1.26	1.09	1.16	0.76
5	1	12	0	250	200	1.00	1.09	0.60	0.55	1.07	1.13	0.91	0.77
6	1	16	0	500	200	1.00	1.10	0.58	0.52	1.08	1.14	0.92	0.77
7	1	14	10	375	200	1.00	1.19	0.56	0.60	1.25	1.08	1.16	0.75
8	1	21	12.5	375	200	1.00	1.19	0.59	0.61	1.23	1.12	1.03	0.76
9	1	17	0	250	200	1.00	1.10	0.59	0.52	1.08	1.14	0.92	0.77
10	1	25	25	250	200	1.00	1.23	0.58	0.61	1.33	1.09	1.26	0.78
11	1	25	0	500	200	1.00	1.14	0.55	0.45	1.13	1.11	0.89	0.71
12	1	21	12.5	375	200	1.00	1.19	0.59	0.61	1.23	1.12	1.03	0.76
13	1	9	5	375	200	1.00	1.14	0.57	0.62	1.20	1.09	1.22	0.78
14	1	9	5	375	200	1.00	1.16	0.58	0.62	1.20	1.10	1.24	0.79
1	2	8	0	250	200								
2	2	10	10	250	200								
3	2	10	0	500	200								
4	2	14	10	375	200								
5	2	12	0	250	200								
6	2	16	0	500	200								
7	2	14	10	375	200								
8	2	21	12.5	375	200								
9	2	17	0	250	200								
10	2	25	25	250	200								
11	2	25	0	500	200								
12	2	21	12.5	375	200								
13	2	9	5	375	200								
14	2	9	5	375	200								

The row indicates the allowable measuring response factor ranges of each gas according to DIN EN 15267-3 (2008) standardization.

Run	Device	Factor 1 A: H_2 mL/min.	Factor 2 B: Air Premixing mL/min.	Factor 3 C: Air Rewind mL/min.	Factor 4 D: Tensile Stress V	Response 1 **Propane** mL/min.	Response 2 **Toluene** mL/min.	Response 3 **n-Butanol** mL/min.	Response 4 **Methyl Acetate** mL/min.	Response 5 **Benzene** mL/min.	Response 6 **Octane** mL/min.	Response 7 **Dichloromethane** mL/min.	Response 8 **Methanol** mL/min.
1	1	10	0	250	220								
2	1	8	10	250	220								
3	1	8	0	500	220								
4	1	10	10	500	220								
5	1	9	5	375	220								
6	1	14	10	375	220								
7	1	9	5	375	220								
8	1	16	0	250	220								
9	1	12	20	250	220								
10	1	12	0	500	220								
11	1	16	20	500	220								
12	1	21	12.5	375	220								
13	1	14	10	375	220								
14	1	25	0	250	220								
15	1	17	25	250	220								
16	1	17	0	500	220								
17	1	25	25	500	220								
18	1	21	12.5	375	220								
1	2	10	0	250	220								
2	2	8	10	250	220								
3	2	8	0	500	220								
4	2	10	10	500	220								
5	2	9	5	375	220								
6	2	14	10	375	220								
7	2	9	5	375	220								
8	2	16	0	250	220								
9	2	12	20	250	220								
10	2	12	0	500	220								
11	2	16	20	500	220								
12	2	21	12.5	375	220								
13	2	14	10	375	220								
14	2	25	0	250	220								
15	2	17	25	250	220								
16	2	17	0	500	220								
17	2	25	25	500	220								
18	2	21	12.5	375	220								

Table 4 Represents the List of experiments to be performed

4.3 Evaluation of DoE

In this section the evaluation process of DoE using Design Expert Software has been discussed in detail. In order to start with the analysis of data provided by SIEMENS as shown in Table 4, Historical Data design is created via the Response Surface tab and Historical Data option. In numeric factor tab 3 factors were selected and were given names as H_2, Air Premixing and Air Rewind. As the runs were only performed at constant value of factor 4 i.e. 200 V, therefore it is left out from the design. As the RSM design was kept at 2-level factor design where each factor requires only minimum and maximum values. The values for H_2 (8-25 mL/min), for Air Premixing (0-25 mL/min) and for Air Rewinding (250 – 500 mL/min) were inserted.

Additionally, the number of rows of data given into the design layout was 14 rows. Once we have selected the setting for factors then we can proceed to response tab. As in the original data set we had response values for 8 gases shown in Table 4, however propane has constant value of 1 for which no analysis could be perform therefore it was left out from responses. The number of responses are defined in the design were then 7, finally a blank design layout with 14 row and 10 column was obtained. The values for factors were then copied from the Table 4 and inserted into factor columns along with their corresponding response values. At this point the Historical Data Design is ready for analysis to extract the hidden information from the given data set.

4.4 Design Summary

The Design Summary tab provide an overview of whole design space, it have been very useful to see either correct values for factors and responses were selected before we start with the analysis. It also gives the detail description of design i.e. type of design, design model, maximum and minimum values of factors and responses and so on. The design summary for the above mentioned DoE is shown below in figure 6.

Design Summary

File Version	7.0.0.1		
Study Type	Response Surface	**Subtype**	Randomized
Design Type	Historical Data	**Runs**	14
Design Model	Quadratic	**Blocks**	No Blocks

Factor	Name	Units	Type	Subtype	Minimum	Maximum	Coded	Values	Mean	Std. Dev.
A	H2	mL/min	Numeric	Continuous	8.00	25.00	-1.000=8.00	1.000=25.00	15.07	5.94
B	Air Premixing	mL/min	Numeric	Continuous	0.00	25.00	-1.000=0.00	1.000=25.00	6.43	7.38
C	Air Rewinding	mL/min	Numeric	Continuous	250.00	500.00	-1.000=250.00	1.000=500.00	357.14	96.29

Response	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio	Trans	Model
R1	Tolune	a.u	14	Polynomial	1.09	1.27	1.15714	0.0563545	1.16514	None	RQuadratic
R2	Butanol	a.u	14	Polynomial	0.55	0.6	0.578571	0.0146009	1.09091	None	RQuadratic
R3	Methyl acetat	a.u	14	Polynomial	0.45	0.63	0.572857	0.0531223	1.4	None	RQuadratic
R4	Benzol	a.u	14	Polynomial	1.07	1.4	1.18643	0.105291	1.30841	None	RQuadratic
R5	Octane	a.u	14	Polynomial	1.08	1.15	1.11214	0.0239161	1.06481	None	RQuadratic
R6	Dichlorometha	a.u	14	Polynomial	0.88	1.67	1.08429	0.221106	1.89773	None	R2FI
R7	Methanol	a.u	14	Polynomial	0.71	0.82	0.768571	0.0238125	1.15493	None	RQuadratic

Figure 6 Design Summary

4.5 Design Analysis

In this chapter the analysis process of the responses in the design for each gas will be shown. The following analysis steps were performed for each gas.

In the fit summary the best mathematical model will be suggested by Design Expert. In this tab the summary, the Sequential Model Sum of Squares [Type I], the Lack of fit Test and the Model Summary Statistics are listed. These values will help to evaluate the model. For "Sequential Model Sum of Squares [Type I]" the highest polynomal order should be selected plus the additional terms have to be significant and the model has not to be aliased. In the table "Lack of Fit Tests" the selected model should have an insignificant lack of fit. In the "Model Summary Statistics" the model maximizing the "Adjusted R-Squared" and the "Predicted R-Squared" is prefered.

In the ANOVA tab the choosen model can be evaluated and analyzed. For that some values have to be considered. Values of "Prob > F" less than 0,0500 indicate model terms are significant. Also the different model terms (e.g A, B, AB, A^2, B^2 and C^2) are listed and are mentioned as significant or not significant. Values greater than 0.1000 indicate the model terms are not significant. Furthermore the "Lack of Fit F-value" shows if the lack of fit is significant or not significant relative to the pure error. It is prefered to have a non-significant lack of fit which means the model

is good. Moreover the "Pred R-Squared" and the "Adj R-Squared" are mentioned. The aim is to have less difference between these values. The value "Adeq Precision" measures the signal to noise ratio where a ratio greater than 4 is prefered. In this case the model can be used to navigate the design space.

The ANOVA tables for each gas are shown in the appendix. For all the gases besides Dichloromethane the quadratic model was choosen. For Dichloromethane the 2FI model was choosen.

In the tab Model Graphs different graphs can be used to interpret and evaluate the choosen model. For each gas three contour plots and one interaction plot were selected individually. For the three contour plots H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min were choosen. The three contour plots were choosen to show the impact and interactions of Air Rewind on the response factor. The interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level at a fixed value for Air Rewind. For all gases besides Butanol, Methyl acetate and Methanol 375 mL/min was selected for Air Rewind in the interaction plots. For Butanol, Methyl acetate and Methanol 250 mL/min was selected for Air Rewind in the interaction plots.

In the following chapter the values and terms of the choosen models, the minimum and maximum values of the response factor of the measurements and the fullfilling ranges in the DIN EN 15267-3 (2008) standardization are mentioned for each gas individually. Also the different plots and the impact of the different factors were explained and discussed for each gas individually.

In the conclusion chapter the results were summerized and recommandations for the improvment and further steps were mentioned also with regard to the opimization chapter.

4.5.1 Analysis for Toluene

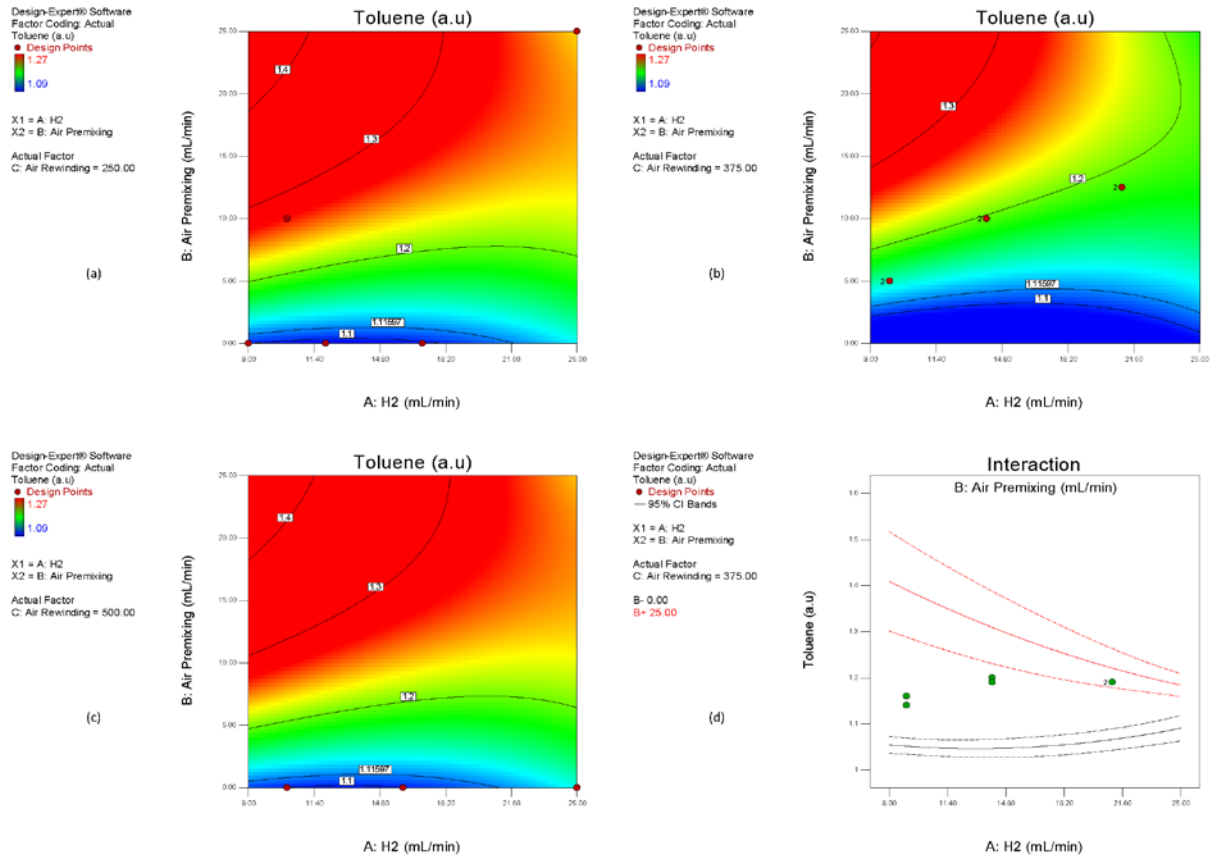

Figure 7 Contour Plots for Toluene

The figure 7 shows three different contour plots for Toluene with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c) respectively. One interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 375 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Toluene is 0,80 to 1,10. For the performed design response factors between 1,09 and 1,27 were measured. On average the aim is to reduce the response factor values to a target value between 0,8 and 1,1.

The contour plots show regions in colours from blue to red for response factor values from 1,09 to 1,27. In order to decrease the response factor values the aim is to increase the blue region. This is achieved by keeping the Air Rewind at 375 mL/min shown in Fig.7 (b).

The interaction plot in Fig. 7(d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 375 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for Toluene was found. At Air Rewinding 375 mL/min the largest region for low response factor values was found. Furthermore a negative trend to lower response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot.

4.5.2 Analysis for Butanol

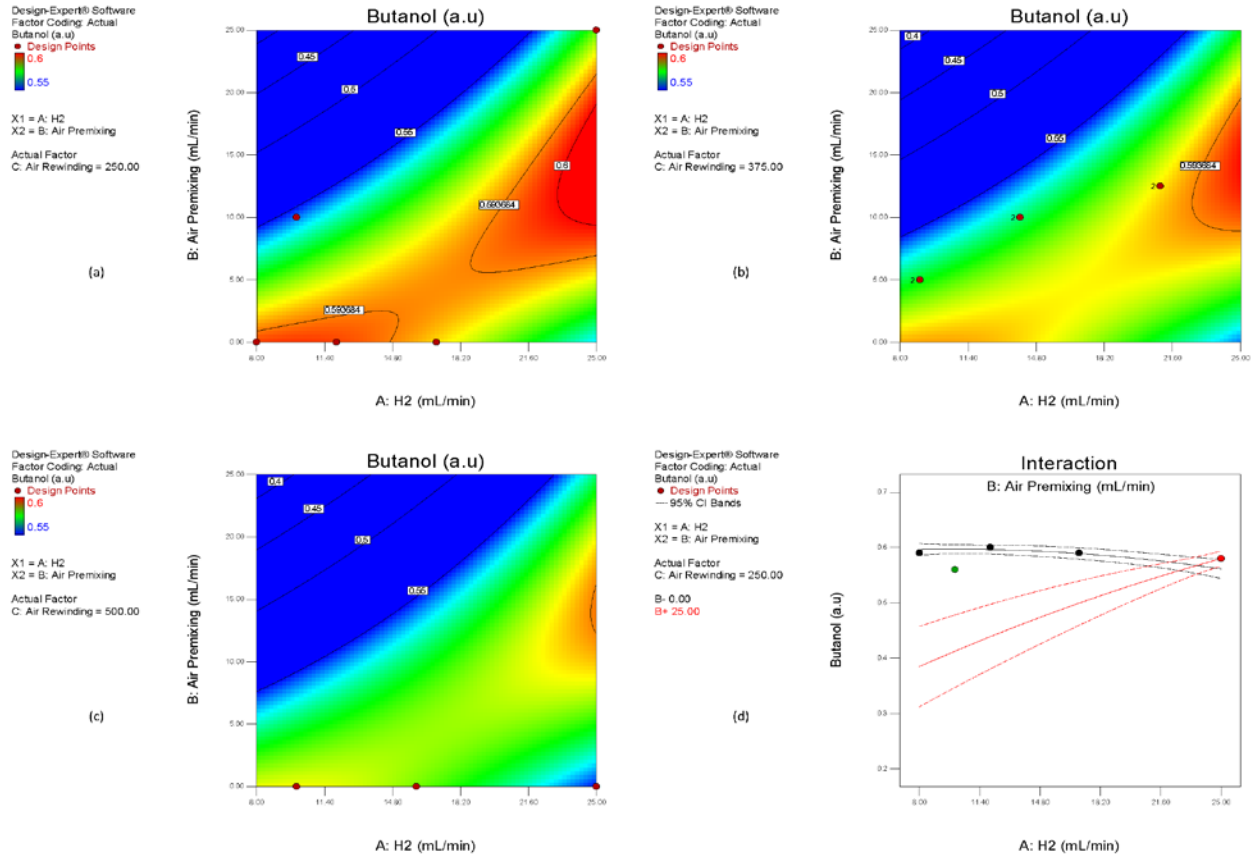

Figure 8 Contour Plots for Butanol

The figure 8 shows three different contour plots for Butanol with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c). One interaction with H_2 in mL/min as X1-axis and the response

factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 250 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Butanol is 0,90 to 1,10. For the performed design response factors between 0,55 and 0,60 were measured. This means no measurement value is in the desired range. For Butanol the aim is to reach at least the lower limit 0,90 according to the DIN EN 15267-3 (2008) standardization. On average the aim is to increase the response factor values to a target value between 0,90 to 1,10.

The contour plots show regions in colours from blue to red for response factor values from 0,55 to 0,60. In order to increase the response factor values the aim is to increase the red region. This is achieved by keeping the Air Rewind at 250 mL/min shown in Fig. 8 (a).

The interaction plot in Fig.8 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve/function) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 250 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for Butanol was found. At Air Rewinding 250 mL/min the largest region for high response factor values was found. Furthermore a positive trend to higher response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot

4.5.3 Analysis of Methyl acetate

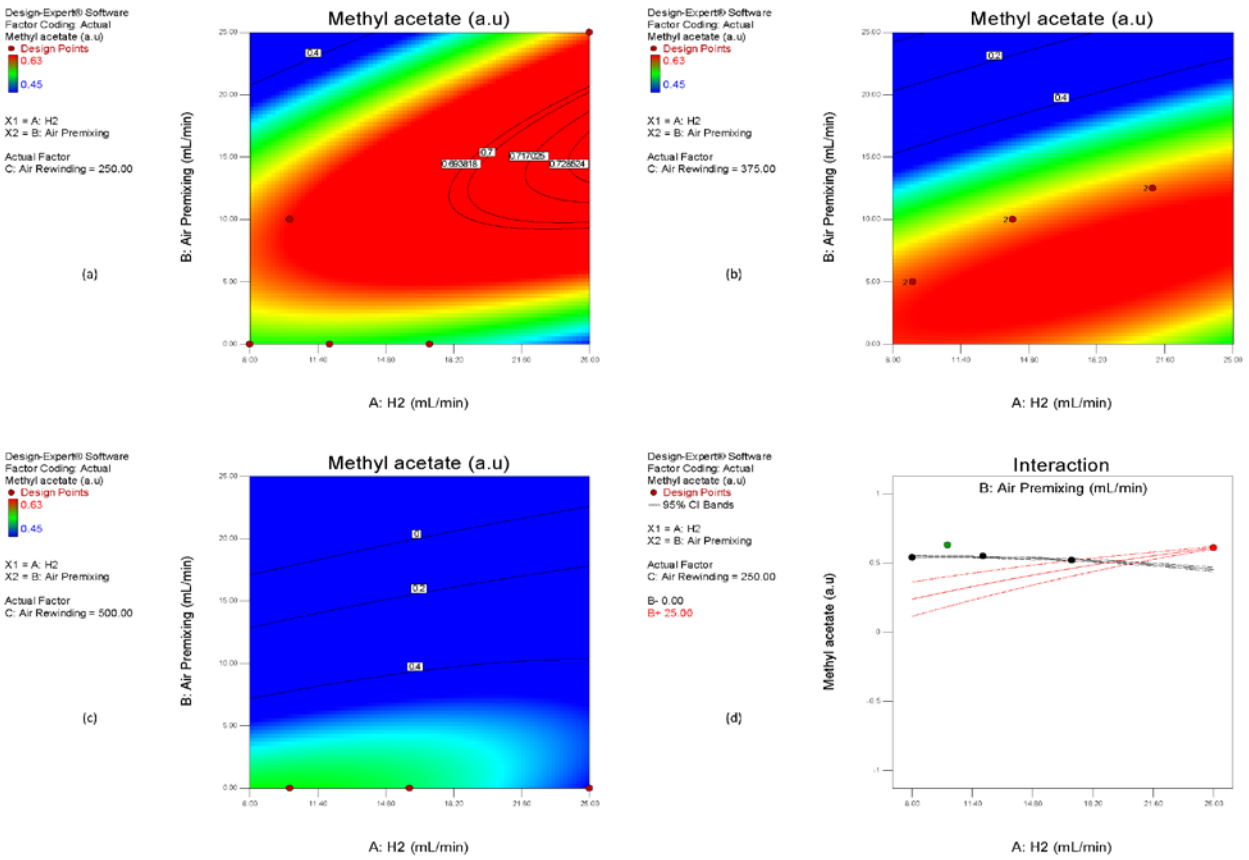

Figure 9 Contour Plots for Butanol

The Figure 9 shows three different contour plots for Methyl acetate with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c). One interaction with H2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 250 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Methyl acetate is 0,70 to 1,00. For the performed design response factors between 0,45 and 0,63 were measured. This means no measurement value is in the desired range. For Methyl acetate the aim is to reach at least the lower limit 0,70 according to the DIN EN 15267-3 (2008) standardization. On average the aim is to increase the response factor values to a target value between 0,70 to 1,00.

The contour plots show regions in colours from blue to red for response factor values from 0,45 to 0,63. In order to increase the response factor values the aim is to increase the red region. This is achieved by keeping the Air Rewind at 250 mL/min shown in Fig. 9 (a).

The interaction plot in Fig. 9 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 250 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for Methyl acetate was found. At Air Rewinding 250 mL/min the largest region for high response factor values was found. Furthermore a positive trend to higher response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot.

4.5.4 Analysis of Benzene

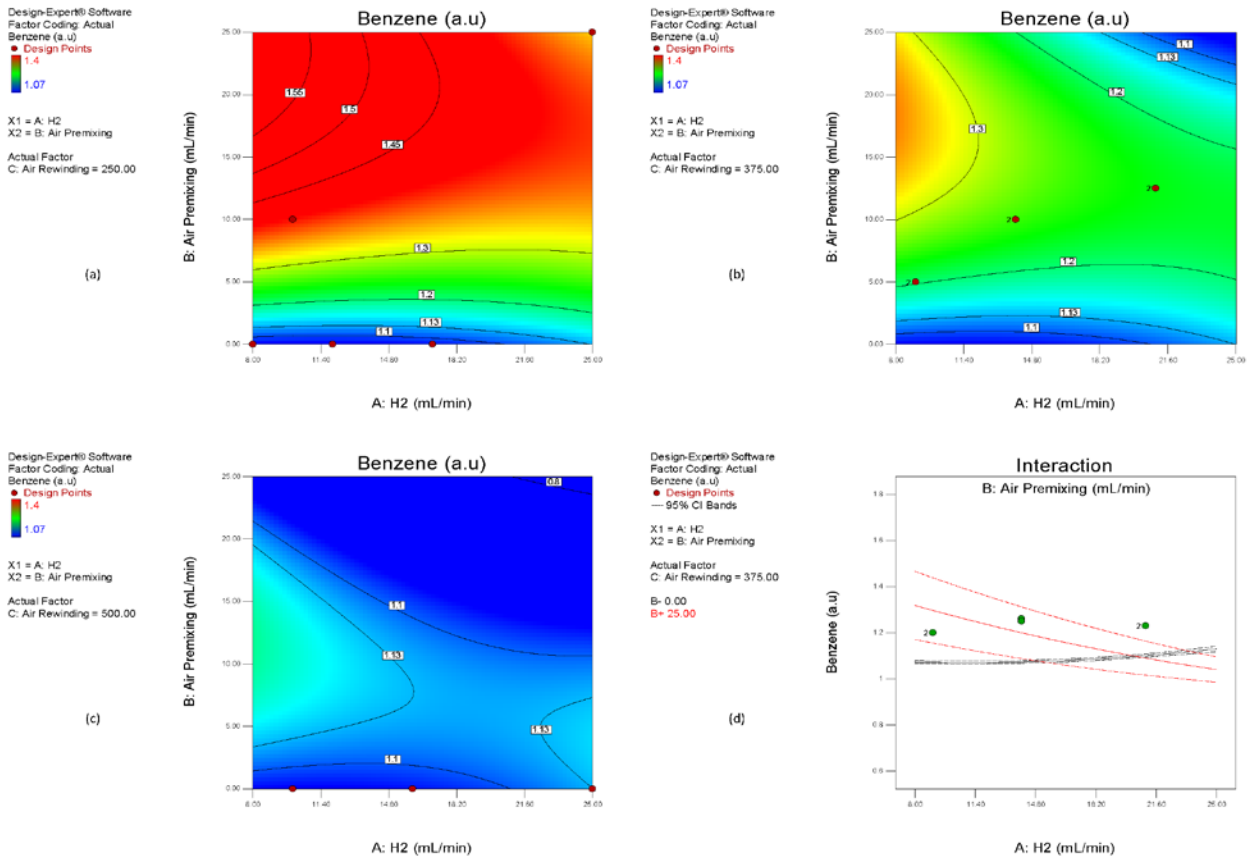

Figure 10 Contour Plots for Benzene

The figure 10 shows three different contour plots for Benzene with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c) respectively. One interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 375 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Benzene is 0,80 to 1,10. For the performed design response factors between 1,07 and 1,40 were measured. On average the aim is to reduce the response factor values to a target value between 0,8 and 1,10.

The contour plots show regions in colours from blue to red for response factor values from 1,07 to 1,40. In order to decrease the response factor values the aim is to increase the blue region. This is achieved by keeping the Air Rewind at 500 mL/min shown in Fig. 10 (c).

The interaction plot in Fig. 10 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve/function) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 375 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for Benzene was found. At Air Rewinding 500 mL/min the largest region for low response factor values was found. Furthermore a negative trend to lower response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot.

4.5.5 Analysis of Octane

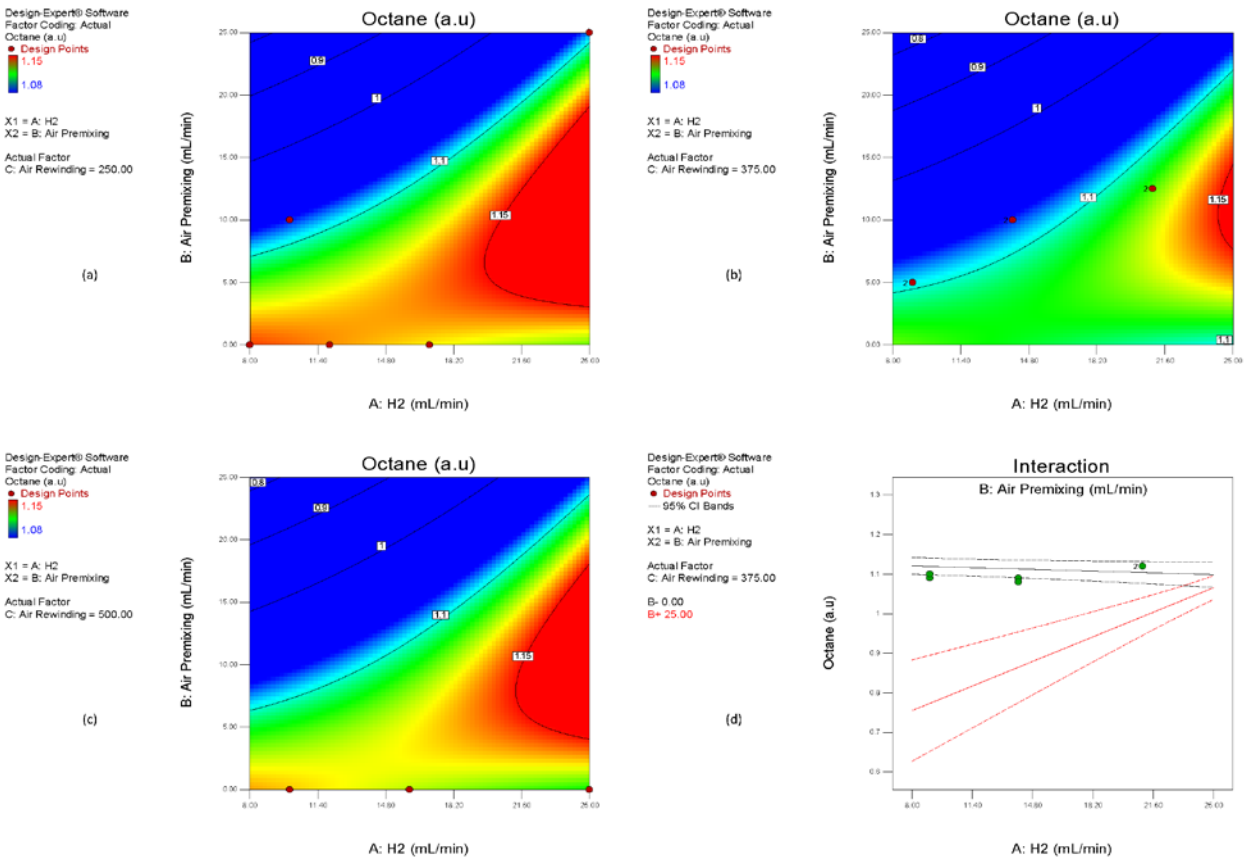

Figure 11 Contour Plots for Octane

The figure 11 shows three different contour plots for Benzene with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c) respectively. One interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 375 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Octane is 0,90 to 1,10. For the performed design response factors between 1,08 and 1,15 were measured. On average the aim is to reduce the response factor values to a target value between 0,90 and 1,10.

The contour plots show regions in colours from blue to red for response factor values from 1,08 to 1,15. In order to decrease the response factor values the aim is to increase the blue region. This is achieved by keeping the Air Rewind at 375 mL/min shown in Fig. 11 (b).

The interaction plot in Fig.11 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve/function) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 375 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for ~~**Benzene**~~ **Octane** was found. At Air Rewinding ~~**500 mL/min**~~ **375 mL/min** the largest region for low response factor values was found. Furthermore a positive trend to higher response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot. The interaction plot also shows that we can work from middle to high values for H_2 to work in the desired range. But at higher values for H_2 the response factor values will be out of range.

4.5.6 Analysis of Dichloromethane

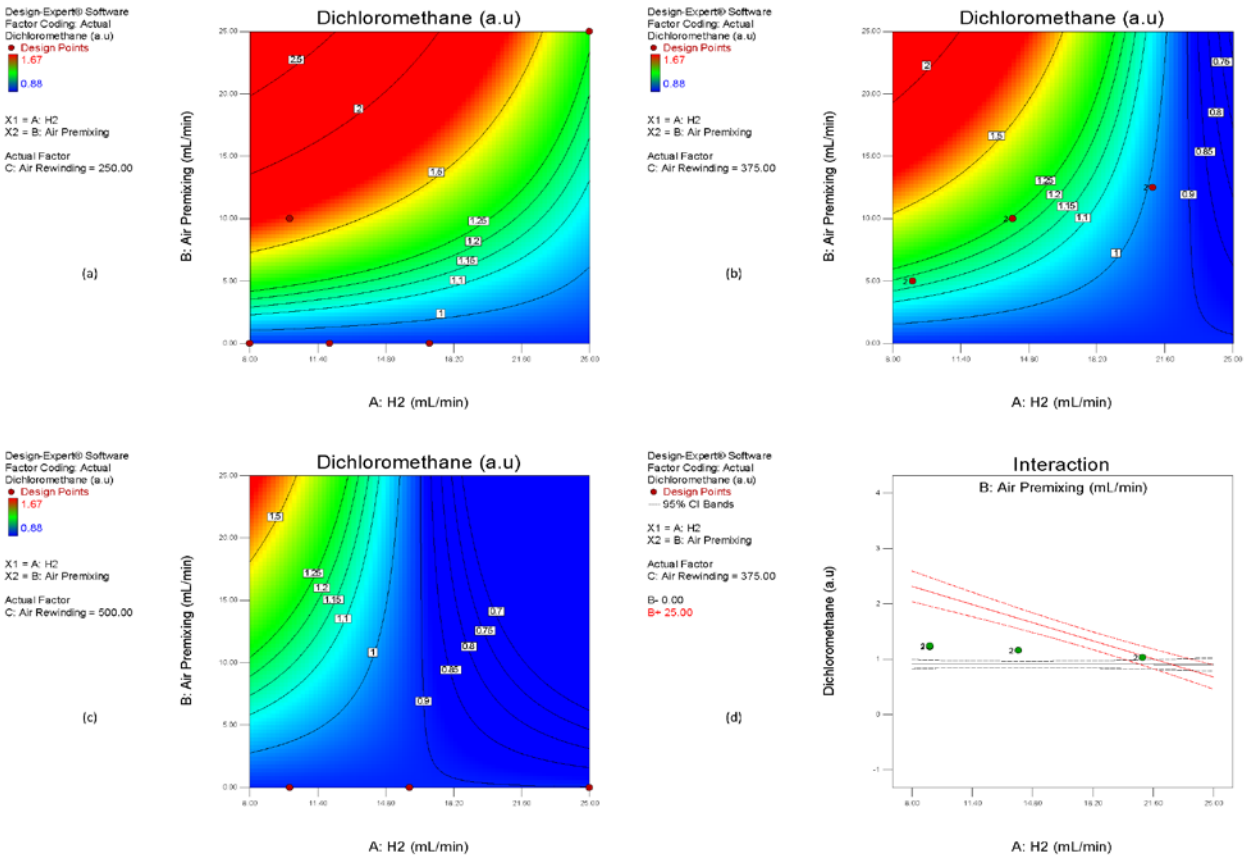

Figure 12 Contour Plots for Dichloromethane

The Figure 12 shows three different contour plots for Dichloromethane with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500

mL/min) for Air Rewind in mL/min (a, b and c) respectively. One interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 375 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Dichloromethane is 0,75 to 1,15. For the performed design response factors between 0,88 and 1,67 were measured. On average the aim is to reduce the response factor values to a target value between 0,75 and 1,15.

The contour plots show regions in colours from blue to red for response factor values from 0,88 to 1,67. In order to decrease the response factor values the aim is to increase the blue region. This is achieved by keeping the Air Rewind at 500 mL/min shown in Fig. 12 (c).

The interaction plot in Fig.12 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve/function) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 375 mL/min is selected for Air Rewind.

According to the contour plots an optimum working range for ~~**Benzene**~~ **Dichloromethane** was found. At Air Rewinding 500 mL/min the largest region for low response factor values was found. Furthermore a negative trend to lower response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot.

4.5.7 Analysis of Methanol

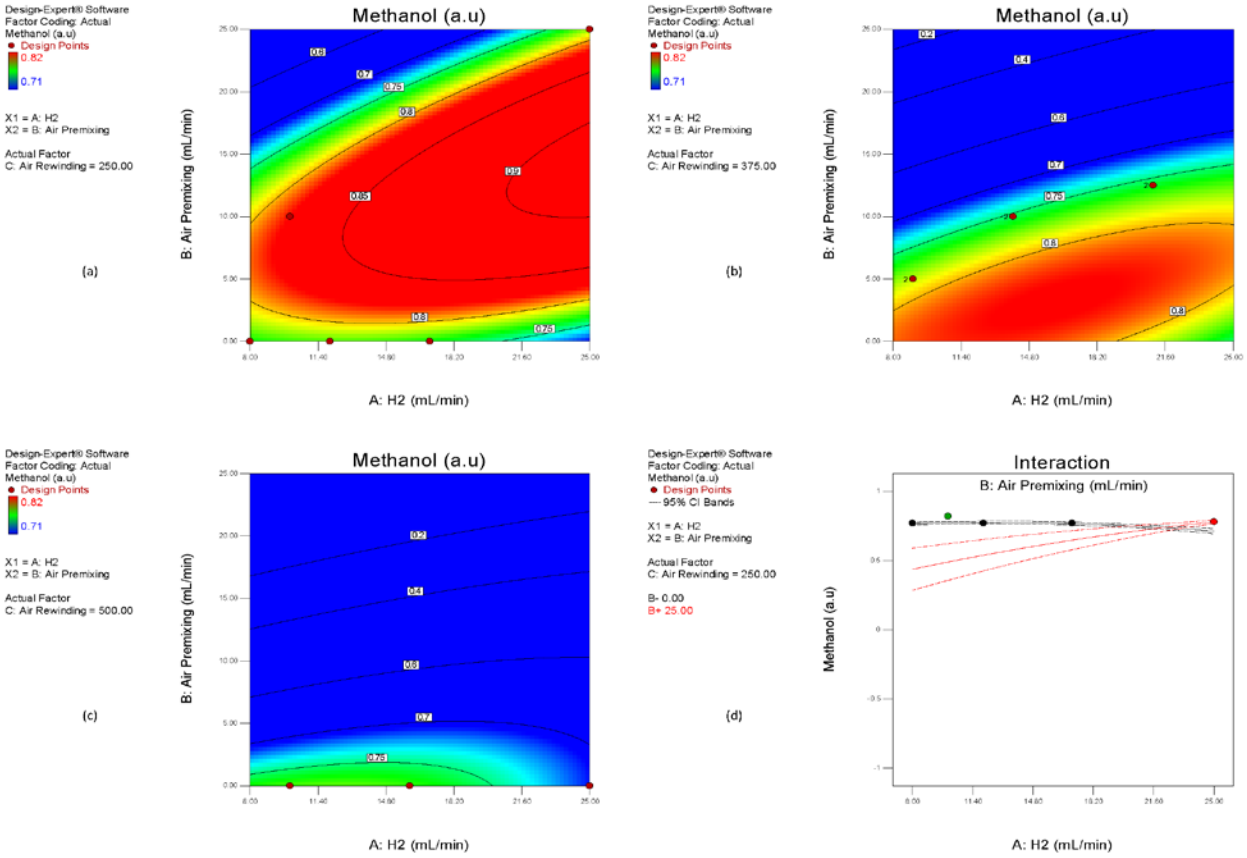

Figure 13 Contour Plots for Methanol

The figure 13 shows three different contour plots for Methanol with H_2 in mL/min as X1-axis and Air Premixing in mL/min as X2-axis and three different levels (250, 375 and 500 mL/min) for Air Rewind in mL/min (a, b and c) respectively. One interaction plot with H_2 in mL/min as X1-axis and the response factor as X2-axis shows the impact and trends of Air Premixing at maximum and minimum level and 250 mL/min selected for Air Rewind (d).

The response factor range according to the DIN EN 15267-3 (2008) standardization for Methanol is 0,70 to 1,00. For the performed design response factors between 0,71 and 0,82 were measured. For Methanol all response factor values are in the desired range. But it has to be mentioned that all response factor values are at the lower limit of the DIN EN 15267-3 (2008) standardization. Therefore on average the aim is to increase the response factor values to a target value between 0,70 and 1,00.

The contour plots show regions in colours from blue to red for response factor values from 0,71 and 0,82. In order to increase the response factor values the aim is to increase the red region. This is achieved by keeping the Air Rewind at 250 mL/min shown in Fig. 13 (a).

The interaction plot in Fig. 13 (d) shows the impact and trend of Air Premixing in mL/min at minimum (black curve) and maximum (red curve/function) with H_2 in mL/min as X1-axis and the response factor as X2-axis. In this case the value 250 mL/min is selected for Air Rewind.

According to the contour and interaction plots an optimum working range for ~~**Benzene**~~ **Methanol** was found. At Air Rewinding 250 mL/min the largest region for low response factor values was found. Furthermore a positive trend to higher response factor values at a maximum level for Air Premixing (red curve) and high values for H_2 was found in the interaction plot.

4.6 Optimization of Design

In this chapter the optimization of the design for further experiments is mentioned. The first step was to select lower and upper limits for both the factors H_2, Air Premixing and Air Rewind and the seven response gases. Furthermore a target value of the response factor was selected. The lower and upper limits for the factors H_2, Air Premixing and Air Rewind were kept at the values from the performed design. For each gas lower and upper limits and a target value were defined individually.

For Butanol and Methyl acetate the lowest measured response factor values were selected as lower limit to ensure that the values are in the design space. For Butanol and Methyl acetate the minimum measured response factor values are 0,55 and 0,45. For the other gases the response factor ranges according to the DIN EN 15267-3 (2008) standardization were selected.

In Table 6 one of the possible solutions set for optimization are represented. These solutions are based on the response factor values from the design and the selected mathematical model. In Table 5 the lower and upper limits and the targets for the factors and responses were mentioned. In the gap "Goal" the desired targets for each gas are shown. For Benzene the "Goal" maximize was selected because the response factor values of the measurements are higher then desired in the DIN EN 15267-3 (2008) standardization. Furthermore this selection was one of the opportunities that provides solutions for this model.

In table 5 solutions with different factor values for H_2, Air Premixing and Air Rewind and the predicted response factor values were shown. In the "Desirability" gap the values decrease from solution 1 to 13 where high values for Desirability are preferred.

It is important to mention that the solutions for optimization are not fixed. The lower and upper limits and the target values can be changed for each factor and response to generate optimal conditions.

In this chapter only numerical optimization solutions were suggested. For graphical optimization no common working ranges to fulfil the DIN EN 15267-3 (2008) standardization for all gases was found.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A:H_2	is in range	8	25	1	1	3
B:Air Premixing	is in range	0	20	1	1	3
C:Air Rewinding	is in range	250	500	1	1	3
Toluene	is target = 1.1	0.8	1.10	1	1	3
Butanol	is target = 0.63	0.55	1.1	1	1	3
Methyl acetate	is target = 0.6	0.45	1	1	1	3
Benzene	maximize	0.8	1.1	1	1	3
Octane	is target = 1.05	0.9	1.1	1	1	3
Dichloromethane	is target = 0.95	0.75	1.15	1	1	3
Methanol	is target = 0.85	0.7	1	1	1	3

Table 5 Numerical optimization parameters

Solutions												
Number	H_2	Air Premixing	Air Rewinding	Toluene	Butanol	Methyl acetate	Benzene	Octane	Dichloromethane	Methanol	Desirability	w/o Intervals
1	25.000	0.000	381.697	1.091	0.556	0.534	1.130	1.099	0.906	0.755	0.304	0.304
2	24.961	0.000	382.592	1.091	0.556	0.535	1.130	1.099	0.906	0.755	0.304	0.304
3	25.000	0.000	384.289	1.091	0.556	0.534	1.130	1.099	0.906	0.754	0.304	0.304
4	24.937	0.000	381.317	1.090	0.556	0.535	1.130	1.099	0.906	0.755	0.304	0.304
5	24.890	0.000	382.374	1.090	0.556	0.536	1.129	1.099	0.906	0.756	0.303	0.303
6	25.000	0.001	378.203	1.091	0.556	0.535	1.130	1.099	0.906	0.755	0.303	0.303
7	24.879	0.000	377.567	1.090	0.557	0.536	1.129	1.099	0.907	0.756	0.301	0.301
8	25.000	0.025	387.305	1.091	0.556	0.534	1.131	1.099	0.906	0.755	0.293	0.293
9	25.000	0.000	398.582	1.093	0.555	0.531	1.130	1.099	0.906	0.753	0.287	0.287
10	25.000	0.000	366.195	1.091	0.556	0.535	1.130	1.099	0.907	0.755	0.284	0.284
11	25.000	0.073	379.917	1.092	0.556	0.536	1.132	1.100	0.906	0.756	0.259	0.259
12	8.911	4.604	396.476	1.144	0.574	0.608	1.186	1.099	1.136	0.775	0.218	0.218
13	8.000	4.433	399.007	1.146	0.572	0.602	1.186	1.098	1.141	0.769	0.202	0.202

Table 6 Numerical Optimization Solutions

4.7 Experimental Runs to Compare Fidas24 and FIDMAT 6 Response Factors

As discussed in the above section that it was not possible to achieve an optimal overlay region where all the response values for selected gases lie within the ranges specified in DIN EN 15267-3(2008). It is also important to note that all the response values for n-Butanol and Methyl acetate were quite lower than the minimum value of standard (as shown in table 4). Therefor it was decided to compare the response values of FIDMAT 6 original device with certified ABB Fidas24 gas Analyser for multiple gases at SEMENS Laboratory in Karlsruhe. For that purpose parallel experimentations were performed on both devices using their built in parameter setting. The results of experiment are shown in table 7, The response values coloured with green are in range for both devise whereas the response values coloured in yellow are out of range specified in DIN EN 15267-3(2008). The results were quite surprising that the ABB Fidas24 shows more response values out of range as compared to the SIEMENS FIDMAT 6. Also it important to note that the response values for n-Butanol and Methyl acetate are similar and out of range for both devices. This shows that also ABB Fidas24 can not fulfil the DIN EN 15267-3 (2008) standardization with regard to the setup at SEMENS Laboratory in Karlsruhe.

ABB FIDAS 24								
GAS-1						Corr.		
			bottle	bottle		reading		reading
sample	formula	C number	Conc / mg	Conc / ppm		mg	limit	mg
nitrogen	N2							-0.125
propane	C3H8	3	296	184	1	15.934		15.809
toluene	C7H8	7	611	163	1.06	16.848	0.80-1.10	16.723
n-butanol	C4H10O	4	482	225	0.61	9.733	0.90 - 1.10	9.608
Methyl ace	C3H6O2	3	469	292	0.57	9.047	0.70-1.00	8.922
benzene	C6H6	6	498	155	1.05	16.663	0.80-1.10	16.538
octane	C8H18	8th	686	160	1.13	17.948	0.90 - 1.10	17.823
DiClorMeth	CH2Cl2	1	561	1047	0.85	13.605	0.75-1.15	13.48
methanol	CH3OH	1	211	394	0.8	12.707	0.70-1.00	12.582
GAS-2								
nitrogen	N2							-0.188
propane	C3H8	3	296	184	1	15.925		15.738
P-xylene	C8H10	8th	801	187	0.87	13.811	0.80-1.10	13.624
chlorobenz	C6H5Cl	6	701	218	0.98	15.62	0.80-1.10	15.433
trichloroeth	C2HCl3	2	824	769	1.01	16.113	0.90 - 1.10	15.925
trichlorome	CHCl3	1	776	1448	0.62	9.827	0.90 - 1.10	9.639
ethylbenze	C8H10	8th	776	181	0.88	13.97	0.80-1.10	13.783
tetrachloro	C2Cl4	2	1032	963	1.1	17.513	0.90 - 1.10	17.326
Ethan	C2H6	2	203	189	1.01	16.011	0.90 - 1.10	15.824
GAS-3								
nitrogen	N2							-0,250
propane	C3H8	3	296	184	1	15.909		15.659
hexane	C6H14	6	182	572	0.86	13.609	0.90 - 1.10	13.359
methane	CH4	1	198	106	1.09	17.344	0.90 - 1.20	17.094
isooctane	C8H18	8th	178	763	1.01	16,010	0.90 - 1.10	15.76
propene	C3H6	3	175	281	0.98	15.658	0.90 - 1.10	15.408
n-butane	C4H10	4	182	390	1.01	16,047	0.90 - 1.10	15.797

SIEMENS FIDAMAT 6								Alt device_1_ID3_Orig
						Corr.		
			bottle	bottle		reading		reading
sample	formula	C number	Conc / mg	Conc / ppm		pA	limit	pA
nitrogen	N2							0.848
propane	C3H8	3	296	184	1	3,652		4,500
toluene	C7H8	7	611	163	1.1	4,027	0.80-1.10	4,875
n-butanol	C4H10O	4	482	225	0.6	2,189	0.90 - 1.10	3,037
Methyl ace	C3H6O2	3	469	292	0.57	2,098	0.70-1.00	2,946
benzene	C6H6	6	498	155	1.1	4,027	0.80-1.10	4,875
octane	C8H18	8th	686	160	1.1	4,029	0.90 - 1.10	4,877
DiClorMeth	CH2Cl2	1	561	1047	0.91	3,329	0.75-1.15	4,177
methanol	CH3OH	1	211	394	0.76	2,758	0.70-1.00	3,606
nitrogen	N2							0.86
propane	C3H8	3	296	184	1	3,646		4,506
P-xylene	C8H10	8th	801	187	0.89	3,239	0.80-1.10	4,099
chlorobenz	C6H5Cl	6	701	218	1.04	3,786	0.80-1.10	4,647
trichloroeth	C2HCl3	2	824	769	1	3,644	0.90 - 1.10	4,504
trichlorome	CHCl3	1	776	1448	0.56	2,055	0.90 - 1.10	2,916
ethylbenze	C8H10	8th	776	181	0.9	3,299	0.80-1.10	4,159
tetrachloro	C2Cl4	2	1032	963	1.07	3,892	0.90 - 1.10	4,752
Ethan	C2H6	2	203	189	1.01	3,676	0.90 - 1.10	4,537
nitrogen	N2							0.863
propane	C3H8	3	296	184	1	3,654		4,517
hexane	C6H14	6	182	572	0.86	3,129	0.90 - 1.10	3,993
methane	CH4	1	198	106	1.1	4,036	0.90 - 1.20	4,899
isooctane	C8H18	8th	178	763	1	3,660	0.90 - 1.10	4,523
propene	C3H6	3	175	281	1	3,671	0.90 - 1.10	4,534
n-butane	C4H10	4	182	390	1.01	3,689	0.90 - 1.10	4,552

Table 7 Comparative study of gas analyzers

5 Conclusion

One aim in this project was to find reasons why the gas analyser FIDAMAT 6 from SIEMENS can not fulfil the response factor ranges for some gases according to DIN EN 15267-3 (2008) standardization and to find possible optimization steps. This was achieved by using Design of Experiments. For each gas the response factor values were analysed to find a model for each gas and to show impacts and trends of the factors H_2, Air Premixing and Air Rewind on the response factor value and to find optimum working parameters. Also possible optimization steps were carried out based on the data analysis. From the data analysis for each gas individually it was found that factor H_2 has to be increased to measure desirable response factor values. Moreover for all gases besides Benzene factor Air Rewind has to be set to lower or middle value to increase the desirable region in the contour plots. For Benzene optimum value for factor Air Rewind is at 500 mL/min. Furthermore 13 solutions for the different factors were carried out in the optimization step. It has to be mentioned that with this analysis of the DoE no adjustments of the different factors were found to fulfil all response factor values at the same time according to DIN EN 15267-3 (2008) standardization.

The experimental runs to compare ABB Fidas24 and SIEMENS FIDAMAT 6 shown that also the ABB device does not fulfil the response factor ranges according to DIN EN 15267-3 (2008) standardization. Possible reasons could be a different set-up in the testing phase when ABB Fidas24 was used to get the certification for DIN EN 15267-3 (2008) standardization. Also different quality of gas supplies could have an effect on the response factor value.

6 Recommendations

From the data analysis of the performed DoE trends for the different factors and the response factor value for the different gases were carried out. More insight from the data analysis were that the factor H_2 has to be increased to measure desirable response factor values plus for all gases besides Benzene factor Air Rewind has to be set to lower or middle value to increase the desirable region in the contour plots. For Benzene optimum value for factor Air Rewind is at 500 mL/min. For further steps a new DoE can be created with regard to the analysed data. For the factors H_2, Air Premixing and Air Rewind the minimum and maximum values can be adjusted according to the

data analysis. In this case the size of the design space of the new DoE will increase plus the analysed trends and optimization steps can be proved. But it has to be considered if the new experiments are able to run on the device after adjusting the minimum and maximum values for the factors. To increase the lack of fit value for the DoE more experiments have to be performed. Plus the distribution of the experiments has to be high when we look on the graph columns of the design. If more runs are added to the DoE make sure to have a good distribution of the runs in the design space. Also cross-verification is possible by using more than one device.

One aim is to focus on the gases Butanol and Methyl acetate (besides Trichloromethane and Hexane) shown in Table 7. With the provided devices it is not possible to measure desirable response factor values for these gases. So it is important to find settings to get the response factor values in the desired range of the DIN EN 15267-3 (2008) standardization. Furthermore one challenge is to find adjustments of the different factors were found to fulfil all response factor values at the same time according to DIN EN 15267-3 (2008) standardization.

As SIEMENS AG Karlsruhe announced that measurements with 215 V for Tensile Stress are running the effect of the 4^{th} factor Tensile Stress can be analyzed. Also the current data set can be included to this analysis. In this case it is important to not overfit the model by to many factors and to less measurements.

If the response factor values can not be fulfilled by adjusting the parameters H_2, Air Premixing, Air Rewind and Tensile Stress other improving steps were required. One improvement step could be another inlet system for the factor Air Premixing to prevent that the flame goes out. The air could be inserted slowly in a linear proportional way to a certain level so flame will be stable. Due to cost it is preferred to keep the method and the conditions of the device and to find adjustments were the desired range can be fulfilled. Another improving step is to change the physics and the hardware of the device, which is costly due to e.g. completely new development steps and material costs.

Finally the setup with the ABB Fidas24 Analyzer and the gas mixing device can be installed in the PA&T department and sample gases and gas mixtures can be measured. Also a new DoE can be created and performed with the supplied gases and with the standard setting of the device.

7 Project Organization

7.1 Working Packages and Milestones

No.	Working Packages and Milestones	Time Span				Expenditure of human labour	
		start	stop	days	working days	man hours	Name
Part A : Task relating to FIDMAT 6 Siemens Gas Analyser							
1	**WP 1: Preparatory work, research** • Research for literature on determination of VOCs/THC using FID method. • Identification of factors influencing FID measurement. • Research for new literature until the end of the project (at least 2 h per week). ***M1:*** 20th May, 2017 Project proposal submission; project goals already clearly defined.	01.04.17	30.07.17	90	75	375	1 2
2	**WP 2: Preparing project documentation and organization** • Preparation of a project outline including: • State of the art. • Gantt-diagram. • Working Packages and Milestones. • Project Based resource planning. ***M2:*** 29th April, 2017 Project proposal submission; project goals already clearly defined.	17.04.17	5.05.17	20	15	75	1 2
3	**WP 3: Evaluation of FIDMAT 6 data obtained from SIEMENS using Design Expert Software.**	10.05.17	10.06.17	30	20	80	1 2

	• Data obtained from SIEMENS will be evaluated using Design-Expert® Software. ***M2:*** The DoE results will identify critical influencing parameters and optimize the operating parameters for FIDMAT 6. ***stop criterion:*** ***Data should be provided by Siemens. If the DoE results are not satisfactory, then the WP 4 will be followed.***						
4	**WP 4: Creating New DoE** • Identification of new parameters and their ranges affecting the response factor and propose new DoE. ***M2:*** The DoE results will identify critical influencing parameters and optimize the operating parameters for FIDMAT 6. ***Stop criterion:*** *Project will not be affected, if the WP 3 and WP4 remain uncomplete.*	10.06.17	20.06.17	30	20	80	1 2
Part B : Task relating to ABB AO2000-FIDAS 24 gas analyzer							
5	**WP 5: Prepare Safety Instructions Manual** • Prepare safety instructions manual for safe operation of FIDAS 24 Gas Analyzer. • Safety Instructions for working with Gases. ***M2:*** *Preparation of safety instruction manual for safe operation* of FIDAS 24 Gas Analyzer. ***Stop criterion:*** *Without achieving this mile stone further working packages cannot be executed.*	10.05.17	12.05.17	02	02	10	1 2
6	**WP 6: Preparation for Installation**	15.05.1	20.05.	05	25	20	1

	This working package include: • Selection of installation site in PAT Lab for FIDAS 24 analyzer. • Preparation of layout for whole system i.e. gas line, gas connections, pressure regulators, flow restrictors etc. • Selection and availability of gases. ***M2:*** *This WP will make sure proper material is available for commissioning and start-up of gas analyzer.* ***stop criterion:*** The delay in achieving this working package will directly influence the overall progress of project.	7	17				2
7	**WP 7: Commissioning of FIDAS 24 Gas Analyser.** This working Package include: • Preparation of gas connection. • Preparation of electrical connection. • Implementation of PC for Data acquisition/storage. • Start-up of Gas Analyser. • Preparation of SoP for FIDAS 24. ***M2:*** *Gas analyzer will be ready to take measurements of sample gases.* ***Stop criterion:*** All the tasks in WP7 must be achieved. Failure in achieving these tasks will result in delay of project.	20.05.17	20.06.17	30	22	88	1 2
8	**WP 8: Determination of TOC of sample gases.** This WP includes: • Selection of suitable gas mixing device. • Gas mixing device will be installed to prepare gas mixtures. • TOC of some gas mixtures will be determined and reported. • Determination of response factors	21.06.17	23.06.17	03	03	15	1 2

	of some available gases. ***M2:*** *Experimental setup will be versatile to measure VOC of various gas mixtures.* ***stop criterion:*** The unavailability of sample gases and gas mixing devices will result in failure of this WP.						
9	**WP 9: Preparation and Submission of Project Report and Project Presentation.** • In this WP all the project work will be documented in the form of project report. Which will be submitted before the project dead line. • After approval of project report, project will be presented. ***M2:*** *Documentation of project work.* ***stop criterion:-***	15.06.17	30.06.17	15	13	50	12

In order to achieve the project goals the whole is divided into two main parts and each part is further divided in to subparts so that project goals could be achieved on time. The progress of first part depends on how fast SIEMENS conduct experiments according to proposed DoE and send response factor values in order to perform analysis using DoE software. In case of unsatisfactory results from DoE software, new factor ranges will be defined and again experiments will be performed so that optimum design space could be achieved.

The second part is related to installation and start-up of ABB AO2000-FIDAS 24 gas analyser. In order to achieve this task timely coordination with the Swagelok will be carried out to make gas connection correctly. The progress of this goal is dependent on delivery of required material and the delay in delivery may halt the installation work.

7.2 Project Time Line (Gantt Chart)

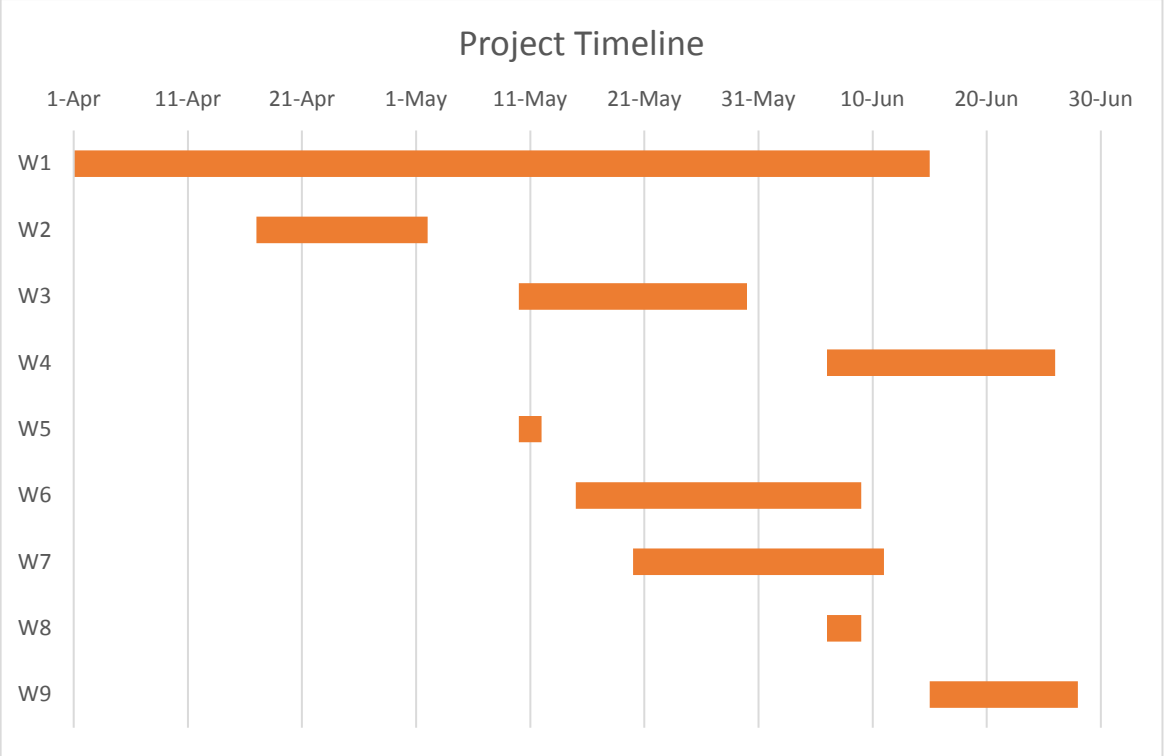

Figure 14 Gantt Chart

8 Project-based Resource Planning

The costs for equipment usage were calculated following the description of “Wegweiser für Forschungsinteressierte- Nutzungsentgelt für Geräte, des RRI, Stand 2009”.

The personal costs were calculated with the values of “Personaldurchschnittsätze der Deutschen Forschungsgemeinschaft (DFG) fürr das Jahr 2008”.

8.1 Costs of Devices

Table 8 Costs of Devices

Device name/ software	Producer	Acquisition value [€]	Charge for use* [€/hr]	Period of use [hr]	Equipment costs [€]
AO2000-FIDAS 24 Software Version: **FIDAS 24: 3.4.2**	**ABB Automation GmbH, Frankfurt**	**40,000**	**8**	**60**	**480**
Burkert Gas Mixer	**Burkert Fluid Control Systems** **USA**	**4,350**	**0.87**	**60**	**52.2**
PC	**Samsung …….**	**800**	**5**	**560**	**2,800**
The Unscrambler	**CAMO Software AS.**	**3.150**	**15**	**50**	**750**
				Total	**4082.00**

*It is calculated by dividing the acquisition cost by 5,000 hr of device active time. This time period is calculated for 10 years of device use by considering 10 hr per week.

8.2 Costs of Materials

Table 9 Costs of materials

Product		Producer	Quantity	Costs [€]
Gas Connections	**SS-6M0-3** T-VERSCHRAUBUNG 6MMX6MMX6 UNION TEE	Swaglok	1	27.30 €
	SS-6M0-1-4RS EINSCHRAUBER 6MM X G1/4 A MALE CONNECTOR	Swaglok	1	12.05 €
	SS-6M0-1-2-DT2 EINSCHRAUBER 6MM X1/8"NPT MIT TEFLONBAND (2X)	Swaglok	5	45.75 €
	SS-6M5-4M STÜTZHÜLSE 6MM X 4MM INSERT	Swaglok	20	54.00 €
	SS-6M0-NFSET MUTTER-KLEMMRING-SATZ 6MM VPE=5 STÜCK	Swaglok	10	46.5 €
	SS-8-HC-A-811 SCHLAUCHTÜLLE 1/2" X 1/2"ROHRSTUTZEN	Swaglok	1	26.80 €
	SS-6M0-6-8 GER.RED.VERSCHR.6MM X 1/2	Swaglok	1	33.85 €
	PFA-T6M-1M-30M PFA SCHLAUCH 6MM X 1MM	Swaglok	1	273.30 €
Gases	Propane (3.5)	Westfalen AG	T12	245.00 €
	Methane(4.5)	Westfalen AG	T10	245.00 €
	Ethane(3.5)	Westfalen AG	T10	385.00 €
	Hydrogen(5.0)	Westfalen AG	T50	39.00 €
	Nitrogen (5.0)	Westfalen AG	T50	21.00 €
	Synthetic Air	Westfalen AG	T50	29.00 €
Total				1456.25 €

8.3 Costs of Employees

Table 10 Costs of employees

Employee	Salary group	Collectively agreed basic salary (in position of Tarifvertrag TV-L, 2008) [€]	Overhead rate (10% of basic salaries)	Costs in total (per month, if 37,5 h per week) [€]	Costs in total (per hour, if 37,5 h per week) [€]
Dorian Segadlo	E10	3.800,00	380,00	4.180,00	39,81
Mahmood Mubarak	E10	3.800,00	380,00	4.180,00	39,81
Prof. Dr. Karsten Rebner	E13	4.900,00	490,00	5.390,00	51,33
MSc. Tobias Drieschner	E13	4.900,00	490,00	5.390,00	51,33
MSc. Mona Stefanakis,	E13	4.900,00	490,00	5.390,00	51,33

8.4 Total Costs of the Project

Table 11 Total Costs of the Project

Type of costs	Price [€]
Costs of devices	4082.00
Costs of materials	1456.25
Costs of employees	24,530.00
Total	**30,068.25**

9 Safety Information:

The operation manual for Advance Optima AO2000 Series ABB specify the instructions for safe operation of Fidas 24 Gas Analyzer, which must be fulfilled by the user. The following are the important point from the operation manual[21]:

- The gas analyzer is suitable for the measurement of flammable gases, but flammable portion should not exceed 15 vol.% CH4 or C1 equivalents.

Instructions followed while installation of gas analyzer:

- The gas analyzer installation work comprise of making electrical and gas connections. The operational manual specifies all the requirements to be fulfilled when connecting the combustion gas and combustion air lines to the gas analyzer.
- The pressures and flow rates of combustion gas and combustion air should not exceed the specified maximum limits.
- In case of H_2 as combustion gas the maximum allowable flow rate is 10 L/hr. For that purpose flow restrictor must be installed as mentioned in manual.
- Normally all the H_2 supply lines in laboratory are installed with **shut-off valve,** in case of installation of gas analyzer to another location make sure that shut-off-valve requirements are full filled.

- When measuring flammable gases, it must be made sure that in case of a failure of the instrument air supply or of the analyzer module itself the sample gas supply to the analyzer module is shut off and the sample gas path is purged with nitrogen.

Instructions to be followed in case of opening the gas connections inside or outside the Gas analyzer:

- The combustion gas feed path in the gas analyzer may not be opened! The combustion gas feed path can become leaky as a result!. Escaping combustion gas can cause fires and explosions, also outside the gas analyzer![21].
- In case combustion gas feed path inside the gas analyzer is opened, seal integrity with a leak detector.
- The seal integrity tests for combustion gas line inside and outside the gas analyzer feed path must be checked on regular basis.

10 Appendix

10.1 Appendix A.1

Run	Device	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2	Response 3	Response 4	Response 5	Response 6	Response 7	Response 8
		A: H_2	B: Air Premixing	C: Air Rewind	D: Tensile Stress	Propane	Toluene	n-Butanol	Methyl Acetate	Benzene	Octane	Dichloromethane	Methanol
		mL/min.	mL/min.	mL/min.	V	mL/min.	mL/min.	mL/min.	mL/min.	mL/min.	mL/min.	mL/min.	mL/min.
1	2	8	0	250	200								
4	2	10	10	250	200								
6	1	10	0	500	200								
7	1	8	10	500	200								
9	1	9	5	375	200								
10	1	9	5	375	200								
13	2	12	0	250	200								
16	2	16	20	250	200								
18	1	16	0	500	200								
19	1	12	20	500	200								
21	1	14	10	375	200								
22	1	14	10	375	200								
25	2	17	0	250	200								
28	2	25	25	250	200								
30	1	25	0	500	200								
31	1	17	25	500	200								
33	1	21	12.5	375	200								
34	1	21	12.5	375	200								
2	1	10	0	250	220								
3	1	8	10	250	220								
5	2	8	0	500	220								
8	2	10	10	500	220								
11	2	9	5	375	220								
12	2	9	5	375	220								
14	1	16	0	250	220								
15	1	12	20	250	220								
17	2	12	0	500	220								
20	2	16	20	500	220								
23	2	14	10	375	220								
24	2	14	10	375	220								
26	1	25	0	250	220								
27	1	17	25	250	220								
29	2	17	0.0	500	220								
32	2	25	25.0	500	220								
35	2	21	12.5	375	220								
36	2	21	12.5	375	220								

Table A 1 Final DoE proposed to Siemens

10.2 Appendix B ANOVA Tables

Response	1	**Toluene**				
ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0,041	7	5,859E-003	129,37	< 0.0001	**significant**
A-H2	1,235E-003	1	1,235E-003	27,28	0,0020	
B-Air Premixing	4,594E-003	1	4,594E-003	101,43	< 0.0001	
C-Air Rewinding	2,230E-005	1	2,230E-005	0,49	0,5091	
AB	1,646E-003	1	1,646E-003	36,34	0,0009	
A^2	7,138E-004	1	7,138E-004	15,76	0,0074	
B^2	4,394E-004	1	4,394E-004	9,70	0,0207	
C^2	1,820E-003	1	1,820E-003	40,19	0,0007	
Residual	2,717E-004	6	4,529E-005			
Lack of Fit	2,174E-005	3	7,248E-006	0,087	0,9625	**not significant**
Pure Error	2,500E-004	3	8,333E-005			
Cor Total	0,041	13				
Std. Dev.	6,730E-003		R-Squared	0,9934		
Mean	1,16		**Adj R-Squared**	**0,9857**		
C.V. %	0,58		**Pred R-Squared**	**0,7174**		
PRESS	0,012		Adeq Precision	34,694		
-2 Log Likelihood	-112,17		BIC	-91,05		
			AICc	-67,37		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1,21	1	3,984E-003	1,20	1,22	
A-H2	-0,047	1	9,046E-003	-0,069	-0,025	11,48
B-Air Premixing	0,11	1	0,011	0,085	0,14	12,39
C-Air Rewinding	2,131E-003	1	3,037E-003	-5,300E-003	9,561E-003	1,57
AB	-0,065	1	0,011	-0,092	-0,039	9,14
A^2	0,022	1	5,604E-003	8,535E-003	0,036	1,31
B^2	-0,046	1	0,015	-0,083	-9,920E-003	14,00
C^2	0,048	1	7,593E-003	0,030	0,067	4,36

Table B 1 Toluene

Table B 2 Butanol

Response	**2**	**Butanol**				
ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2,536E-003	6	4,227E-004	12,56	0,0019	**significant**
A-H2	1,066E-003	1	1,066E-003	31,70	0,0008	
B-Air Premixing	1,010E-003	1	1,010E-003	30,02	0,0009	
C-Air Rewinding	1,544E-004	1	1,544E-004	4,59	0,0694	
AB	1,673E-003	1	1,673E-003	49,74	0,0002	
A^2	1,880E-004	1	1,880E-004	5,59	0,0500	
B^2	5,215E-004	1	5,215E-004	15,50	0,0056	
Residual	2,355E-004	7	3,364E-005			
Lack of Fit	1,355E-004	4	3,387E-005	1,02	0,5156	**not significant**
Pure Error	1,000E-004	3	3,333E-005			
Cor Total	2,771E-003	13				
Std. Dev.	5,800E-003		R-Squared	0,9150		
Mean	0,58		**Adj R-Squared**	**0,8422**		
C.V. %	1,00		**Pred R-Squared**	**0,5434**		
PRESS	1,266E-003		Adeq Precision	11,160		
-2 Log Likelihood	-114,17		BIC	-95,70		
			AICc	-81,50		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0,57	1	3,305E-003	0,56	0,58	
A-H2	0,040	1	7,102E-003	0,023	0,057	9,52
B-Air Premixing	-0,048	1	8,806E-003	-0,069	-0,027	10,46
C-Air Rewinding	-5,293E-003	1	2,470E-003	-0,011	5,481E-004	1,40
AB	0,058	1	8,164E-003	0,038	0,077	6,98
A^2	-0,011	1	4,816E-003	-0,023	3,031E-006	1,31
B^2	-0,034	1	8,564E-003	-0,054	-0,013	6,26

Table B 3 Methyl Acetate

Response	**3**	**Methyl acetate**				
ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0,037	8	4,573E-003	233,03	< 0.0001	**significant**
A-H2	6,803E-004	1	6,803E-004	34,66	0,0020	
B-Air Premixing	1,059E-003	1	1,059E-003	53,98	0,0007	
C-Air Rewinding	1,765E-003	1	1,765E-003	89,91	0,0002	
AB	1,733E-003	1	1,733E-003	88,31	0,0002	
BC	1,693E-003	1	1,693E-003	86,27	0,0002	
A^2	7,317E-004	1	7,317E-004	37,28	0,0017	
B^2	2,087E-003	1	2,087E-003	106,31	0,0001	
C^2	1,661E-003	1	1,661E-003	84,64	0,0003	
Residual	9,813E-005	5	1,963E-005			
Lack of Fit	9,813E-005	2	4,907E-005			**N/A**
Pure Error	0,000	3	0,000			
Cor Total	0,037	13				
Std. Dev.	4,430E-003		R-Squared	0,9973		
Mean	0,57		**Adj R-Squared**	**0,9930**		
C.V. %	0,77		**Pred R-Squared**	**N/A**		
PRESS	N/A		Adeq Precision	50,992		
-2 Log Likelihood	-126,43		BIC	-102,67		
			AICc	-63,43		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0,58	1	5,119E-003	0,57	0,59	
A-H2	0,070	1	0,012	0,040	0,10	46,38
B-Air Premixing	-0,22	1	0,030	-0,30	-0,14	205,79
C-Air Rewinding	-0,18	1	0,019	-0,23	-0,13	149,26
AB	0,12	1	0,012	0,084	0,15	26,90
BC	-0,18	1	0,020	-0,23	-0,13	136,35
A^2	-0,027	1	4,368E-003	-0,038	-0,015	1,84
B^2	-0,19	1	0,019	-0,24	-0,15	51,52
C^2	-0,083	1	9,001E-003	-0,11	-0,060	14,15

Table B 4 Octane

Response	**5**	**Octane**			
ANOVA for Response Surface Reduced Quadratic model					
Analysis of variance table [Partial sum of squares - Type III]					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	6,939E-003	6	1,156E-003	16,29	0,0009	**significant**
A-H2	3,061E-003	1	3,061E-003	43,12	0,0003	
B-Air Premixing	4,014E-003	1	4,014E-003	56,54	0,0001	
C-Air Rewinding	5,923E-005	1	5,923E-005	0,83	0,3914	
AB	2,725E-003	1	2,725E-003	38,39	0,0004	
B^2	1,162E-003	1	1,162E-003	16,37	0,0049	
C^2	3,385E-004	1	3,385E-004	4,77	0,0653	
Residual	4,970E-004	7	7,100E-005			
Lack of Fit	3,970E-004	4	9,924E-005	2,98	0,1984	**not significant**
Pure Error	1,000E-004	3	3,333E-005			
Cor Total	7,436E-003	13				
Std. Dev.	8,426E-003		R-Squared	0,9332		
Mean	1,11		**Adj R-Squared**	**0,8759**		
C.V. %	0,76		**Pred R-Squared**	**-1,2075**		
PRESS	0,016		Adeq Precision	10,783		
-2 Log Likelihood	-103,71		BIC	-85,24		
			AICc	-71,05		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1,08	1	4,081E-003	1,07	1,09	
A-H2	0,072	1	0,011	0,046	0,098	10,82
B-Air Premixing	-0,100	1	0,013	-0,13	-0,068	11,25
C-Air Rewinding	-3,457E-003	1	3,785E-003	-0,012	5,493E-003	1,56
AB	0,083	1	0,013	0,051	0,11	8,95
B^2	-0,072	1	0,018	-0,11	-0,030	12,79
C^2	0,021	1	9,481E-003	-1,718E-003	0,043	4,34

Response	**4**	**Benzene**				
ANOVA for Response Surface Reduced Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0,14	7	0,021	993,54	< 0.0001	**significant**
A-H2	6,655E-004	1	6,655E-004	32,14	0,0013	
B-Air Premixing	7,570E-005	1	7,570E-005	3,66	0,1044	
C-Air Rewinding	3,841E-003	1	3,841E-003	185,49	< 0.0001	
AB	1,250E-003	1	1,250E-003	60,39	0,0002	
BC	3,482E-003	1	3,482E-003	168,19	< 0.0001	
A^2	6,493E-004	1	6,493E-004	31,36	0,0014	
B^2	1,335E-003	1	1,335E-003	64,47	0,0002	
Residual	1,242E-004	6	2,070E-005			
Lack of Fit	7,423E-005	3	2,474E-005	1,48	0,3766	**not significant**
Pure Error	5,000E-005	3	1,667E-005			
Cor Total	0,14	13				
Std. Dev.	4,550E-003		R-Squared	0,9991		
Mean	1,19		**Adj R-Squared**	**0,9981**		
C.V. %	0,38		**Pred R-Squared**	**0,9078**		
PRESS	0,013		Adeq Precision	95,377		
-2 Log Likelihood	-123,12		BIC	-102,01		
			AICc	-78,32		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1,25	1	4,051E-003	1,24	1,26	
A-H2	-0,055	1	9,766E-003	-0,079	-0,031	29,26
B-Air Premixing	0,039	1	0,020	-0,011	0,088	89,29
C-Air Rewinding	-0,15	1	0,011	-0,17	-0,12	42,42
AB	-0,084	1	0,011	-0,11	-0,057	19,66
BC	-0,14	1	0,011	-0,17	-0,12	42,05
A^2	0,022	1	3,936E-003	0,012	0,032	1,42
B^2	-0,13	1	0,017	-0,18	-0,093	38,92

Table B 5 Benzene

Table B 6 Dichloromethane

Response	**6**	**Dichloromethane**				
ANOVA for Response Surface Reduced 2FI model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0,61	5	0,12	35,96	< 0.0001	**significant**
A-H2	0,38	1	0,38	111,32	< 0.0001	
B-Air Premixing	0,15	1	0,15	45,76	0,0001	
C-Air Rewinding	0,12	1	0,12	34,63	0,0004	
AB	0,23	1	0,23	68,22	< 0.0001	
BC	0,11	1	0,11	32,61	0,0004	
Residual	0,027	8	3,384E-003			
Lack of Fit	0,027	5	5,375E-003	80,63	0,0021	**significant**
Pure Error	2,000E-004	3	6,667E-005			
Cor Total	0,64	13				
Std. Dev.	0,058		R-Squared	0,9574		
Mean	1,08		**Adj R-Squared**	**0,9308**		
C.V. %	5,37		**Pred R-Squared**	**0,7298**		
PRESS	0,17		Adeq Precision	19,300		
-2 Log Likelihood	-47,74		BIC	-31,91		
			AICc	-23,74		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1,20	1	0,032	1,13	1,28	
A-H2	-0,41	1	0,039	-0,50	-0,32	2,85
B-Air Premixing	0,29	1	0,044	0,19	0,39	2,54
C-Air Rewinding	-0,30	1	0,051	-0,42	-0,18	5,89
AB	-0,41	1	0,049	-0,52	-0,29	2,54
BC	-0,30	1	0,052	-0,41	-0,18	5,52

Response	**7**	**Methanol**			
ANOVA for Response Surface Reduced Quadratic model					
Analysis of variance table [Partial sum of squares - Type III]					
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	7,225E-003	8	9,031E-004	30,82	0,0008	**significant**
A-H2	7,121E-004	1	7,121E-004	24,30	0,0044	
B-Air Premixing	1,356E-003	1	1,356E-003	46,30	0,0010	
C-Air Rewinding	1,738E-003	1	1,738E-003	59,31	0,0006	
AB	1,292E-003	1	1,292E-003	44,09	0,0012	
BC	1,705E-003	1	1,705E-003	58,18	0,0006	
A^2	8,638E-004	1	8,638E-004	29,48	0,0029	
B^2	1,558E-003	1	1,558E-003	53,16	0,0008	
C^2	4,454E-004	1	4,454E-004	15,20	0,0114	
Residual	1,465E-004	5	2,930E-005			
Lack of Fit	4,650E-005	2	2,325E-005	0,70	0,5640	**not significant**
Pure Error	1,000E-004	3	3,333E-005			
Cor Total	7,371E-003	13				
Std. Dev.	5,413E-003		R-Squared	0,9801		
Mean	0,77		**Adj R-Squared**	**0,9483**		
C.V. %	0,70		**Pred R-Squared**	**N/A**		
PRESS	N/A		Adeq Precision	25,167		
-2 Log Likelihood	-120,82		BIC	-97,06		
			AICc	-57,82		
Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0,73	1	6,254E-003	0,71	0,75	
A-H2	0,072	1	0,015	0,035	0,11	46,38
B-Air Premixing	-0,25	1	0,036	-0,34	-0,15	205,79
C-Air Rewinding	-0,18	1	0,024	-0,24	-0,12	149,26
AB	0,099	1	0,015	0,061	0,14	26,90
BC	-0,18	1	0,024	-0,24	-0,12	136,35
A^2	-0,029	1	5,337E-003	-0,043	-0,015	1,84
B^2	-0,17	1	0,023	-0,23	-0,11	51,52
C^2	-0,043	1	0,011	-0,071	-0,015	14,15

Table B 7 Methanol

11 References

1. Agency, U.S.E.P., *"Volatile Organic Compounds Emissions."*, in *Report on the Environment*. 2011.
2. Wolkoff, P.W., C. K.; Clausen, P. A.; Nielsen, G. D., *Organic compounds in office environments - sensory irritation, odor, measurements and the role of reactive chemistry.* Indoor Air, 2006. **16**(1): p. 7–19.
3. THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION, *DIRECTIVE (EU) 2016/2284*, in *Official Journal of the European Union*. 2016.
4. Instruments®Corporation, C. *How to Select a Total Hydrocarbon Analyzer for use in an Industrial Application*. Document APP014 2006; Available from: www.controlinstruments.com.
5. SIEMENS AG Industry Sector Sensors and Communication, K., Germany, *Reliability and efficiency in continuous gas analysis: A strong family for your success*. 2012.
6. *Master Thesis: "Performance analysis of extractive SIEMENS gas analyzer based on FID working principle in response to air quality and air pollution control towards standardization of DIN EN 15267-3 (2008)"*.
7. I.G. William, R.A.D., in: D.H. Desty (Ed.), Proc. 2nd Symp. Gas Chromatogr. Discussion Group, Butterworth, London, 1958
8. *DIN EN 12619:2013, Stationary source emissions-Determination of the mass concentration of total gaseous organic carbon –Continuous flame ionisation detector method*.
9. Blades, A.T., *The Flame Ionization Detector*. Journal of Chromatographic Science, 1973. **Vol 11**: p. 251-255.
10. Holm, T., *Aspects of the mechanism of the flame ionization detector.* Journal of Chromatography 1999. **A**(842): p. 221–227.
11. DEWAR, R.A., *The flame ionization detector a theoretical approach.* J. Chromatog. , 1961. **6**: p. 312-323.
12. El-Naggar, A.Y., *Factors Affecting Linearity and Response of Flame Ionization Detector*. Petroleum Science and Technology,, 2006. **24**: p. 41-50.
13. M. Dressler, M.C., *Effect of detector temperature on the flame ionization detector response* Journal of Chromatography (1994) 299-305, 1994. **A**(679): p. 299-305.
14. Wai K. Cheng *t, T.S.a.N.C., *The fast-response flame ionization detector*. Prog. Energy Combust. SoL 1998. **24**: p. 89-124,.
15. Karasek, H.Y.T.a.F.W., *Flame Ionization Detector Response Factors for Compound Classes in Quantitative Analysis of Complex Organic Mixtures.* Analytical chemistry, 1984. **56**(12).
16. *Performance Standards and Test Procedures for Continuous Emission Monitoring Systems. For gaseous, particulate and flow-rate monitoring systems, Environment Agency* June 2016. **Version 3.5**.
17. *Ehrler, Oli T. FIDAMAT 6 – Certification for emission monitoring accrdg. EN 15267-3 (2008). Presentation for project FIDAMAT 6. Karlsruhe: SIEMENS AG, PD PA AP R&D DH-KHE, 2016.*
18. *http://www.raeco.com/products/gas-analyzers/Siemens-Fidamat-6/siemens-fidamat-6-man-06-07.pdf*.
19. SIEMENS AG. siemens.com. [Online] FIDAMAT 6, 1996 - 2016. [Cited: 11 15, 2016.] https://w3.siemens.com/mcms/sensor-systems/en/process-analytics/gas-analyzer-gas-analysis/extractive/hydrocarbons-total-content-measurement/Pages/fidamat-6.aspx.
20. *Serajuddin, Md. and Sreenivas, T. Application of response surface method of optimization in flocculant assisted filtration of uranium bearing alkaline leach slurry of limestone origin. [Publication] Begumpet, India: Published by Maney on behalf of the Institute and The AusIMM, 2015. DOI: 10.1179/1743285515Y.0000000003.*
21. *Advance Optima Continuous Gas Analyzers AO2000 Series, Operator's Manual, 42/24-10 EN Rev. 10.*