

**Standardization of BigOxy method for e-fuel like  
Methanol, Gasoline, and their blends**

**Sweekruth Mysore Sriram**

Thesis to obtain the Master of Science Degree in

**Energy Engineering and Management**

Supervisors: Prof. Duarte de Mesquita e Sousa  
Eng. Chandra Kanth Kosuru

**Examination Committee**

Chairperson: Prof. Francisco Manuel da Silva Lemos

Supervisor: Prof. Duarte de Mesquita e Sousa

Member of the Committee: Prof. Nuno Henrique Varela Canha

**October 2022**



I declare that this document is an original work of my own authorship and that it fulfils  
all the requirements of the Code of Conduct and Good Practices of the  
*Universidade de Lisboa.*



# Acknowledgements

*I whole heartedly thank my parents who constantly supported me, believed in me and motivated me in every walk of my life. Whatever I am today is because of their love and support. I dedicate this work to my parents.*

*I would like to thank Tec4fuels for giving me this precious opportunity to create this thesis, supporting me and guiding me throughout the process of thesis creation. I whole heartedly thank my supervisor from Tec4fuels, Mr. Chandra Kanth Kosuru for his commitment and support to bring out the best from me and guiding me in every way to contribute to this interesting topic and concoct this report.*

*I am thankful to my supervisor from Instituto Superior Tecnico (IST), Prof. Duarte de Mesquita e Sousa for supporting me from university throughout the process, helping me to complete it successfully with his guidance and obliging with me whenever needed with patience and commitment.*

*My special thanks to Mr. Shamsundar, founder of NIE-CREST (Centre for Renewable Energy and Sustainable Technology), Mysuru, India who was the main reason for me to get this opportunity through his network and support.*

*I express my gratitude to InnoEnergy Master School for providing me this amazing opportunity and international learning experience through dual master's degree program. I believe that the skill sets and experiences that I gained during my dual masters will serve as an asset to my career and my entire life.*

*I am very blessed, honoured, and grateful to each and every one mentioned above for guiding me and supporting me.*

Thank You,

Sweekruth Sriram



# Abstract

Ageing in liquid fuels is a well know phenomenon over the past years. The principle behind ageing in all types of liquid fuels is the auto-oxidation reaction which involves free radical mechanisms. The unsaturated fuel molecules react with the atmospheric oxygen by breaking their bonds. This leads to the formation of acids, ketones, alcohol, and higher chain molecules in the liquid phase which are undesirable. This ability of the fuel to age over time depends on the quality of the fuel. Some fuels may take few months to degrade while some samples can age with in few days. Tec4Fuels GmbH in Aachen, Germany has developed an accelerated ageing method called “BigOxy” that can age fuel samples (both diesel and gasoline fuels) in shorter amount of time. This is achieved by inducing stressful conditions to the fuel samples leading to the accelerated auto-oxidation reaction. Thus, this method has the potential to check the long-term behaviour of the fuels in shorter time frames, especially the novel fuels like alcohol blends, MTG (methanol to gasoline), methanol, etc., In current thesis work, this accelerated ageing method is applied for the methanol, gasoline and their M15 blends. The oxygen consumption in the auto-oxidation reaction is calculated for each fuel to identify its absorption capability. After ageing process, the changes in the quality and oxidation stability behaviour of the fuels are analyzed by performing several analytical tests like water content, acid content and petroOxy for the aged and fresh fuel samples before and after BigOxy ageing.

## Keywords

Accelerated Ageing, Oxidation Stability, BigOxy ageing, Gasoline, Methanol, Induction Period.

# Resumo

O envelhecimento em combustíveis líquidos é um fenômeno bem conhecido nos últimos anos. O envelhecimento em todos os tipos de combustíveis líquidos é devido à reação de auto-oxidação que envolve mecanismos de radicais livres. As moléculas de combustível insaturadas reagem com o oxigênio atmosférico rompendo as suas ligações. Isso leva à formação de ácidos, cetonas, álcool e cadeias de moléculas na fase líquida que são indesejáveis. O processo de envelhecimento do combustível ao longo do tempo depende da qualidade do mesmo. Alguns combustíveis podem levar alguns meses para se degradar enquanto algumas amostras podem envelhecer em poucos dias. A Tec4Fuels GmbH em Aachen, Alemanha, desenvolveu um método de envelhecimento acelerado chamado "BigOxy" de forma a testar o envelhecimento de amostras de combustível (diesel e gasolina) em menos tempo. Isto é conseguido induzindo condições que conduzem à reação de auto-oxidação de forma acelerada. Assim, este método tem o potencial de verificar o comportamento de longo prazo dos combustíveis em prazos mais curtos, especialmente os novos combustíveis como misturas de álcool, MTG (metanol à gasolina), metanol, etc. Nesta dissertação, este método de envelhecimento acelerado é aplicado para o metanol, gasolina e misturas dos mesmos. O consumo de oxigênio na reação de auto-oxidação é calculado para cada combustível para identificar sua capacidade de absorção. Após o processo de envelhecimento, as mudanças na qualidade e comportamento de estabilidade à oxidação dos combustíveis é analisado através da realização de vários testes analíticos às quantidades de água, ácido e estabilidade da oxidação para as amostras de combustível originais e envelhecidas e antes e após o envelhecimento pelo método "BigOxy".

## Palavras-chave

Envelhecimento Acelerado, Estabilidade à Oxidação, Gasolina, Metanol, Período de Indução





# Table of Contents

Acknowledgements .....	v
Abstract .....	vii
Keywords.....	vii
Resumo .....	viii
Palavras-chave.....	viii
Table of Contents .....	x
List of Tables .....	xiii
List of Figures .....	xiv
Nomenclature .....	xv
List of Software.....	xviii
Chapter:1.....	1
Literature review and Background .....	1
1.1    Overview.....	2
1.2    Properties of Liquid Fuel.....	3
1.3    Introduction to electro-fuels (e-fuels) .....	5
1.3.1    Methanol as an e-fuel: .....	5
Chapter: 2.....	7
Accelerated Ageing: Oxidation Stability Test Methods and State of the Art .....	7
2.1    Auto-oxidation in Fuels .....	8
2.1.1    Initiation Reaction: .....	8
2.1.2    Propagation Reaction: .....	9
2.1.3    Termination Reaction:.....	9
2.2    Additives and Stabilizers.....	10
2.2.1    Chemistry of Antioxidants: .....	11
2.3    Accelerated Ageing .....	12
2.4    The BigOxy Test Bench.....	13

2.4.1	BigOxy Experimental Procedure:.....	16
2.4.2	Data Analysis:.....	17
2.4.3	Fluid Analysis:.....	19
2.4.4	Compatibility and Reproducibility:.....	19
2.4.5	Applications of BigOxy:.....	20
2.5	The PetroOxy Method .....	21
2.5.1	Test procedure and apparatus:.....	21
2.5.2	Applications and advantages:.....	22
2.6	The Rancimat Method .....	23
2.6.1	Test procedure and apparatus:.....	23
2.6.2	Applications and advantages:.....	24
2.7	Laboratory Analytics .....	24
2.7.1	Water Content:.....	25
2.7.2	Acid Content: .....	25
2.7.3	Oxidation Stability: .....	26
2.7.4	Density and Viscosity:.....	27
Chapter: 3.....		28
Aim and Methodology .....		28
3.1	BigOxy vs Rancimat and PetroOxy .....	29
3.2	Fuels used for experiments and analysis .....	32
3.2.1	Gasoline, Pure methanol (M100) and Blend of Gasoline with Methanol (M15):.....	32
3.2.2	Fresh fuel samples: .....	33
3.3	Methodology and Approach.....	34
Chapter: 4.....		36
Results and Discussions .....		36
3.4	Results for 24 h BigOxy Experiments .....	36
3.4.1	Gasoline A: .....	36
3.4.2	Gasoline B: .....	37
3.4.3	M 100:.....	38
3.4.4	M15 Gasoline A: .....	38
3.4.5	M15 Gasoline B: .....	39
3.5	Results for 48 h BigOxy Experiments .....	40
3.5.1	Gasoline A: .....	40

3.5.2	Gasoline B: .....	40
3.5.3	M100:.....	41
3.5.4	M15 Gasoline A: .....	42
3.5.5	M15 Gasoline B: .....	43
3.6	Results for 72 h BigOxy Experiments .....	44
3.6.1	Gasoline A: .....	44
3.6.2	Gasoline B: .....	44
3.6.3	M100:.....	45
3.6.4	M15 Gasoline A: .....	45
3.6.5	M15 Gasoline B: .....	46
3.7	Oxygen Consumption Calculation .....	47
3.8	Results for PetroOxy Oxidation Stability.....	49
3.9	Results for Water Content .....	50
3.10	Results for Acid Content.....	53
Chapter: 5.....		56
Conclusion and Future works .....		56
Bibliography.....		59
Annexe 1 .....		63
Annexe 2 .....		67

# List of Tables

Table 1 Comparison of BigOxy with PetroOxy and Rancimat methods.....	31
Table 2 Oxygen consumption of fuels with respect to their ageing periods.....	48

# List of Figures

Figure 1 Piping and instrumentation diagram of BigOxy test bench .....	14
Figure 2 Interior of the BigOxy reactor .....	15
Figure 3 Components of BigOxy reactor .....	15
Figure 4 Pressure curve of the BigOxy experiment .....	18
Figure 5 Temperature Curve of the BigOxy experiment .....	18
Figure 6 The PetroOxy apparatus .....	21
Figure 7 The Rancimat apparatus with measuring positions .....	23
Figure 8 Gasoline A aged for 24 h in BigOxy method .....	37
Figure 9 M100 aged for 24 h in BigOxy method .....	38
Figure 10 M15 Gasoline A aged for 24 h in BigOxy method .....	39
Figure 11 M15 Gasoline B aged for 24 h in BigOxy method .....	40
Figure 12 Gasoline B aged for 48 h in BigOxy method .....	41
Figure 13 M15 Gasoline A aged for 48 h in BigOxy method .....	42
Figure 14 M15 Gasoline B aged for 48 h in BigOxy method .....	43
Figure 15 Gasoline A aged for 72 h in BigOxy method .....	44
Figure 16 Results of PetroOxy Oxidation Stability .....	50
Figure 17 Water Content of the fuels .....	53
Figure 18 Acid Content of the fuels .....	55
Figure 19 Gasoline B aged for 24 h in BigOxy method .....	63
Figure 20 Gasoline A aged for 48 h in BigOxy method .....	63
Figure 21 M100 aged for 48 h in BigOxy method .....	64
Figure 22 Gasoline B aged for 72 h in BigOxy method .....	64
Figure 23 M100 aged for 72 h in BigOxy method .....	65
Figure 24 M15 Gasoline A aged for 72 h in BigOxy method .....	65
Figure 25 M15 Gasoline B aged for 72 h in BigOxy method .....	66

# Nomenclature

<b>AC</b>	Acid Content
<b>AH</b>	Antioxidant
<b>Al<sub>2</sub>O<sub>3</sub></b>	Aluminium Oxide
<b>ASTM</b>	American Society for Testing and Materials
<b>BHA</b>	Butylated Hydroxyanisole
<b>BHT</b>	Butylated Hydroxytoluene
<b>B100</b>	100 % (vol) Biodiesel
<b>CN</b>	Cetane Number
<b>DME</b>	Dimethyl Ether
<b>DMFC</b>	Direct Methanol Fuel Cell
<b>DIN</b>	Deutsches Institut für Normung (German Institute for Standardisation)
<b>E-fuel</b>	Electro fuel
<b>EN</b>	European Norm
<b>FAME</b>	Fatty Acid Methyl Ester
<b>FCV</b>	Fuel Cell Vehicle
<b>FKM</b>	Fluoroelastomer
<b>GHG</b>	Greenhouse Gas
<b>GTL</b>	Gas to Liquid
<b>HVO</b>	Hydrotreated Vegetable Oil
<b>IC</b>	Internal Combustion
<b>ISO</b>	International Standard Organization

<b>LPG</b>	Liquified Petroleum Gas
<b>m<sub>dry air</sub></b>	Amount of dry air in grams
<b>MeOH</b>	Methanol
<b>MTG</b>	Methanol to Gasoline
<b>M100</b>	100 % (vol) Methanol
<b>M15 Gasoline A</b>	15 % vol Methanol in 85% vol Gasoline A
<b>M15 Gasoline B</b>	15 % vol Methanol in 85% vol Gasoline B
<b>M15</b>	15 % vol Methanol
<b>n</b>	Amount of Gas
<b>n<sub>dry air</sub></b>	Amount of dry air
<b>NO<sub>x</sub></b>	Nitrogen Oxide
<b><i>n<sub>O<sub>2</sub>initial</sub></i></b>	Amount of oxygen inside the reactor in initial phase
<b><i>n<sub>O<sub>2</sub>max</sub></i></b>	Amount of oxygen inside the reactor in maximum phase
<b><i>n<sub>O<sub>2</sub>final</sub></i></b>	Amount of oxygen inside the reactor in final phase
<b><i>n<sub>O<sub>2</sub>consumed</sub></i></b>	Amount of Oxygen consumed by the fuel
<b><i>n<sub>O<sub>2</sub>remaining</sub></i></b>	Amount of Oxygen remaining inside the reactor
<b>OME</b>	Oxymethylene Ether
<b>PG</b>	Propyl Gallate
<b>PY</b>	Pyrogallol
<b>P<sub>act</sub></b>	Actual Pressure



<b>P<sub>max</sub></b>	Pressure in the Maximum phase
<b>P<sub>initial</sub></b>	Pressure in the initial phase
<b>P<sub>final</sub></b>	Pressure in the final phase
<b>R</b>	Universal Gas Constant
<b>SO<sub>x</sub></b>	Sulphur Oxide
<b>SVM</b>	Strabinger Viscometer
<b>TBHQ</b>	Tetra Butyl Hydroquinone
<b>TiO<sub>3</sub></b>	Titanium Oxide
<b>T<sub>initial</sub></b>	Temperature in the initial phase
<b>T<sub>max</sub></b>	Temperature in the Maximum phase
<b>T<sub>final</sub></b>	Temperature in the final phase
<b>WC</b>	Water Content
<b>% of O<sub>2</sub><sub>consumed</sub></b>	Percentage of Oxygen consumed by the fuel

# List of Software

<b>MS Excel</b>	To plot all the Graphs for the results of BigOxy experiments and Analytics. To calculate the Oxygen Consumption of fuels
<b>Grafana</b>	To compare and extract the real time temperature and pressure data for all the BigOxy experiments
<b>Edraw Max</b>	To construct the Piping and instrumentation Diagram for BigOxy Apparatus

# Chapter:1

## Literature review and Background

This chapter is the outcome of the literature review conducted to introduce the reader to the main aim of the thesis. The motive of this chapter is to give a detailed overview of the basic concepts required to understand further concepts discussed. This chapter gives a clear introduction to the topic of this thesis. The qualitative aspects required for liquid fuel and its state of the art is explained. The introduction to the ageing phenomenon in liquid fuels is explained, and the influences of the ageing towards fuel applications is also discussed. The accelerated ageing method, that is mainly used for this thesis, is introduced. The important properties of the liquid fuel which is affected by ageing is discussed. Introduction to the electro fuels (e-fuels) and their advantages with respect to environment and performance is elaborated. The e-fuel which is mainly used in this is Methanol. The sources for methanol production are discussed. The advantages of methanol over other e-fuels are also discussed. The advantages of using methanol and blending methanol with gasoline to use as automobile fuel is discussed.

# 1.1 Overview

Petroleum fuels have remained affordable from nearly hundred years since we started using them. Considering the recent years, the prices have been hiking and the availability is going down due to political and economic crisis [1]. Along with this, there is one major concern: environmental pollution or air pollution, which is one of the serious threats to our planet. The greenhouse effect which is caused due to the high emission of carbon dioxide into the atmosphere results in global warming. The effect of particulate matter that is being added to atmosphere due to combustion of fossil fuels is also one of the main reasons for environmental degradation. These particulate matters are very hazardous for our health and other living beings as well. Therefore, this led to the development of alternate or renewable fuels which gained attraction of scientists. Although, the usage of the fossil fuels did not stop, on the contrary the demand was continuously raising. In 1970s, due to the severe rise of petroleum prices along with their usage, several governments and scientific communities pressurized to accelerate research on the feasibility of 'alcohol economy' for fuel production [1].

The demand for liquid fuels is increasing day by day. Along with this it is also very important to maintain the quality of the fuels. Likewise, the qualitative criteria are proportionally getting more stringent. EU has initiated the strict guidelines like Fuel Quality Directive (FQD) and European Environmental Agency (EEA) – they have imposed strict guidelines to maintain the quality of the fuel. The main aim is about guaranteeing the quality of the liquid fuels during long term storage [2]. Generally, the liquid fuels are expected to be of high quality and also, they should be highly stable towards external environment. But, in reality, liquid fuels also do undergo ageing over the period of time when they are stored for longer durations, may be in months or in years, based on their quality. The quality of the fuels starts deteriorating slowly even in the atmospheric storage conditions. One of the main reasons for this is the reaction of liquid fuels with atmospheric oxygen. This oxidation phenomenon is called "Fuel Degradation". There are several parameters which are responsible for this ageing process like temperature, pressure, chemical structure of the fuels, material of the storage tanks, chemical stability of the fuels etc [2] [3]. These quality changes affect the performance characteristics of the fuels and this is mainly observed in the first-generation biofuels [2].

In this thesis report, the methods used to study the ageing phenomenon, and factors responsible for the ageing of gasoline, e-fuels, and their blends are discussed. Generally, the liquid fluids take months or years to age in natural conditions depending on their quality. But Tec4Fuels GmbH company has developed a test method which can age the fuel in the span of hours (24 h, 48 h, 72 h, 96 h etc) which saves lot of time and helps to analyse the factors influencing the ageing. Through this, we can check the compatibility of the fuel towards the long-term storage. The test method is called “BigOxy”, this test bench [4] is used to study the oxidation stability of the fuels like diesel, paraffinic fuels, biodiesel, gasoline and lubricant fluids. This is done by studying the influence of pressure, temperature, and stabilizers on ageing of fuels. There are various accelerated ageing and analytical methods in the market like PetroOxy [5], Rancimat [6], Carbonyl titrations [7] etc., where some of them are discussed below in the further part of this report. In this thesis, the BigOxy method is used, as it offers a wider scope and flexibility for investigating the fuel sample in larger volumes when compared to other ageing methods. One of the main objectives of this thesis is to understand the usability of BigOxy test bench for fuels like gasoline, methanol and their blends. Therefore, discussed in this report, the oxidation stability test results and discussions of BigOxy ageing for fuels like Gasoline, liquid Methanol as an e-fuel (M100) and blend of Methanol with Gasoline (M15).

## 1.2 Properties of Liquid Fuel

All the liquid fuels are energy generating molecules which are combustible, and that energy is converted into mechanical energy like kinetic energy etc. Some of the important properties of the liquid fuels are viscosity, density, heating value, flash point, acid value, cetane number and etc. The quality of the fuel depends on these properties. There are certain engineering standards set to determine the quality of the fuels like ASTM, EN, ISO and etc., to standardize the limits of the fuel properties [2]. These properties vary for every fuel due it’s chemical and physical composition. Some of the important properties with respect to ageing of fuels are listed below.

- Acid content value is the measurement of acidity. It is determined by the amount of potassium hydroxide (mg), which is a strong base, required to neutralize the

free acid content in 1 mg of fuel. It is also the measure of potassium hydroxide (mg) that is required to neutralize the free fatty acid contained in unit mass (g) of chemical substance [3]. This parameter is used to determine the quality of the fuel [8] and sometimes, the acidity of the fuel can be unsuitable against certain materials (engine components) as well. Acid content value is also used to determine the rate of quality degradation in the fuels caused due to ageing as it is an ageing product.

- The Water content of liquid fuel is the solubility limit of water in the fuel. It is an important parameter to maintain the quality of the liquid fuel which reduces the corrosion risks [2].
- The factors influencing chemical structures of the fuel like, The Octane number/Octane value is one of the critical factors to determine the gasoline's performance, it is the resistance of the fuel to completely ignite or to knock [9]. Cetane number (CN) for diesel is used to study ignition quality [8]. These are the parameters used to characterize the fuel ability to undergo combustion without any knocking phenomenon in normal combustion conditions.
- The reaction stability which is also called as oxidation stability, defines the resistance of the fuel towards auto-oxidation reaction and it is used to determine the fuel's quality [2]. This will be discussed in detail in the further chapters.
- The fuel qualities like clarity, corrosion, emulsion forming, filter plugging, and microbial growth can be affected by the water content and the mechanical impurities in the fuel [2].
- The important physical properties are density and viscosity, they characterize the fuel flow through pipes, filters and nozzles. The lubrication properties are responsible to avoid the wear and tear in the fuel systems [8] [3] [2].

These are some of the important properties of the fuel which is used to determine the quality of the fuel and it may change based on the critical factors and storage conditions [2]. It is very important to deliver good quality fuels to the end user with proper instructions about specific storage conditions. The quality of the fuels also depends on the raw materials and methods that are used during their refining process, because it varies for each fuel like petroleum-based fuels, biofuels and etc. Alongside, the storage conditions also play an important role.

## 1.3 Introduction to electro-fuels (e-fuels)

As the pollution rates are increasing severely due to usage of fossil fuels and there is severe need to shift to alternative fuels or green fuels. E-fuels are considered as potential future fuels capable of replacing fossil fuels and can influence in pollution reduction for wellness of our posterity.

Plants convert solar energy into chemical energy through photosynthesis and this chemical energy from plants can be converted into biofuels. But this method requires very large amount of land and sunlight, and the overall efficiency of this method is very low. Therefore, scientists came up with alternative procedures to manufacture these fuels in a non-photosynthetic way more efficiently with means of technology. These fuels are referred to as “e-fuels or electro fuels” [10]. E-fuels are the means to store energy (energy carriers), as well as used as transportation fuels. The energy density of e-fuels is higher than gasoline [11] but, they are expensive and non-compatible. There are mainly two principles followed in the production of e-fuels: First one is biological method of CO<sub>2</sub> conversion to energy dense fuels and the second one is producing fuel by combination of recycled CO<sub>2</sub> and hydrogen which is produced from water electrolysis [10]. Some of the electro fuels are Methanol, Ethanol, DME (dimethyl ether), Butanol, Hydrogen, Ammonia, OME (oxymethylene ether) etc [10].

Alcohols are considered as the best alternative for petroleum fuels for transportation sector. Fuels like bio-ethanol, methanol and butanol gained their importance even during 1970's oil crisis [12]. In current 21<sup>st</sup> century, alcohols are getting even more attention due to its clean fuel qualities, and it can be produced using locally available less used energy resources like biomass and organic wastes. Currently, focussed application of alcohols is mixing them with gasoline for the purpose of reducing the emissions, and reducing the fossil content by oxygenating the fuel [12]. Methanol blends can increase energy conversion efficiencies of the fuel with high octane rating [13]. Importantly, the feedstock for methanol doesn't affect or compete with food consumption [12]. Methanol is a starting product for many e-fuels, and is also used in hydrogen, ammonia and DME productions.

### 1.3.1 Methanol as an e-fuel:

Methanol (CH<sub>3</sub>OH) or Methyl alcohol (MeOH) is one of the simplest of alcohols and is

a colourless liquid having a bit pungent odour. Normally methanol was used as feedstock and as an industrial solvent. Methanol is considered as one of the very important platforms for chemicals where several fuels and additives can be derived from it by further chemical processing. In recent days, Methanol is considered as one of the future transportation fuel [14], which can be used alone or mixed with gasoline. When methanol mixed with, gasoline or any other fossil fuel, it is considered less toxic in terms of emission of pollutants, because the emissions coming from its combustion have reduced carbon content,  $\text{NO}_x$ ,  $\text{SO}_x$  and other particulate matters [14]. Since methanol is a hydrogen carrier, it can also be used in automotive field for the fuel cell vehicle (FCV) development [14].

Liquid methanol is becoming very popular in the energy storage field and [14] is proposed as an alternative to the hydrogen economy. Because, “hydrogen” requires extra storage and transportation technologies [10], [15]. Therefore, methanol is considered as an efficient fuel to promote the use of renewables and to enable energy transition from fossil fuels. Some of the promising applications of methanol are DME (Dimethyl Ether) production, hydrogen production and direct methanol fuel cell (DMFC) [14].



# Chapter: 2

## **Accelerated Ageing: Oxidation Stability Test Methods and State of the Art**

The compatibility of a fuel for long-term storage is determined as the long-term storage stability of the fuel. This can be characterized by various chemical properties of the fuel and its standard storage conditions etc. Oxidation stability is considered as one of the ideal parameters for determining long term storage stability. Oxidation stability is the main reason for ageing phenomenon in fuels. In this chapter, the oxidation reaction mechanism in liquid fuels is discussed. The long-term storage stability behaviour varies for each and every fuel, and it is very hard to determine and conclude that there is one important parameter which is highly sensitive and responsible for ageing in the fuels. This is due to the fuel's chemical structures, and it varies for each fuel type. Therefore, there are several processes or analytical methods to determine the storage stability of the liquid fuels like gasoline, diesel and other fuels derived from mineral oils. In this chapter, the methods used to determine the oxidation stability and method used for accelerated ageing of the liquid fuels are discussed. The analytical methods used to determine the important parameters of the fuel are also discussed with their test procedures.

## 2.1 Auto-oxidation in Fuels

Fuels undergo a slow uncontrollable oxidation process which occurs even in stable storage environment, and it is called as “Self-oxidation or Auto-oxidation”. Especially, for the products which are extracted from the deep processing of the petroleum, we can see the importance of the auto-oxidation, which is one of the main reasons for deterioration of the fuel quality.

The stability of the fuels is determined by their ability to resist auto-oxidation process especially during the storage and it varies for every fuel due to different chemical compositions. The presence of sulphur, nitrogen, traces of metal ions and compounds having hetero oxygen atoms in fuels catalyze the oxidation process. The external storage physical conditions like temperature, accessibility of the light and affinity to oxygen also play an important role. The hydrocarbons which are the main composition of petroleum fuels are most likely to react with each other and with the atmospheric oxygen. The products derived from oxygenation can undergo more changes leading to the decolouration, gum formation, deposit, or sediment formations. Although there are many theories for auto-oxidation in liquid hydrocarbons, but the most significant one is which includes formation of peroxide and hydrocarbon radicals involving chain reaction mechanisms [16].

The Radical mechanisms involves dissolved oxygen in the process of auto-oxidation. The reactions are classified into Initiation, Propagation and Termination reactions. The moment when the fuel is in contact with the atmospheric oxygen through air, it starts reacting by forming free radicals due to the diffusion of the oxygen [16], [17]. This initiates and propagates the reaction further leading to formation of higher molecular structures.

### 2.1.1 Initiation Reaction:



The first step in exothermic auto-oxidation reaction is called initiation reaction and it is the slowest reaction that forms  $\text{R} \cdot$ , which is the hydrocarbon alkyl radical as shown in reactions (1) and (2). Generally, the initiation chemical reaction is the one which triggers the secondary reactions. Auto-oxidation reaction will occur slowly in room

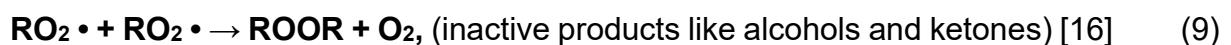
temperature and accelerates in higher temperatures. The bonding energy between the carbon and hydrogen is high which implies the need of higher temperatures to break the bond quicker.

### 2.1.2 Propagation Reaction:



The propagation reaction is the second stage of reaction in auto-oxidation mechanism. Here the (R •) alkyl radicals that are formed in initiation will rapidly react with dissolved oxygen which will form (ROO•) the peroxide radical as shown in the reaction (3). Then the peroxide radical reacts with fuel (RH) to form with the hydroperoxide radical (ROOH) as shown in reaction (4). The hydroperoxide radical decomposes leading to the formation of alkoxy (RO•) and hydroxyl (•OH) active radicals [17] as shown in reaction (5). This will further lead to the separation of the hydrogen atoms from the hydrocarbons which results in the formation of ketones, aldehydes, acid and alcohols which affects performance of the fuels in a negative way. The propagation reaction is fast and self-propagated compared to initiation.

### 2.1.3 Termination Reaction:



The last stage reaction in the auto-oxidation mechanism is termination reaction. Here the two free radicals (R •) and (RO<sub>2</sub> •) will react with themselves leading to the decomposition of hydroperoxides (ROOH) to non-radical products like ketones, alcohols and acids which may further react resulting in the formation of polymers or

macromolecular chains.

The primary C-H bonds of the alkaline is difficult to undergo oxidation when compared to the secondary and tertiary C-H bonds. Generally, the resistance to oxidation is less in the presence of the double bond. For an instance, the weak bonds like unsaturated fatty acids can undergo the thermal oxidative degradation. But cycloalkanes and alkanes have high bonding energies of the C-H bonds which is nearly equal to 413 kJ/mol [18], where the resistance to oxidation is more. This implies that we need higher temperature to break the bonds. There are suitable temperature and pressure conditions for the auto-oxidation reaction to happen and this also depends on the type of the fuel and its quality. Some of the other factors which influences the oxidation reaction by forming free radicals are light, catalysts like metal ions, microorganisms, and water [16].

The temperature range for the auto-oxidation to occur is around 30°C-120°C [16]. As the initial auto-oxidation rate is slow, because the availability of the free radicals is small and as a result the changes occur slowly [2] [10] [4]. The oxidation rate is high and rapid after the induction period because of the intermediate products like acids, aldehydes and ketones which causes the autocatalytic effect, and accumulates through branching chain reaction by forming heavy molecules [16].

## 2.2 Additives and Stabilizers

The performance qualities of the fuels can be maintained and also enhanced by the use of certain chemical substances. Fuel additives are the chemical substances that are added to the fuels to improve its various properties like combustion, boost octane levels, resistance to corrosion, improve storage stability (antioxidants) and increase performance etc. Additives alter the chemical properties of the fuel which enables it to give better performance without altering the engine technology [19]. Using additives is a very cost-effective way of improving the performance of the fuels and addressing the issues associated. There are several types of additives that we use depending on the requirement. Some of them are solid additives, liquid additives and nano additives. There are many categories in additives depending upon their purpose and usage. Ethanol will reduce NO<sub>x</sub> emissions when it is added with biodiesel, nano additives like Al<sub>2</sub>O<sub>3</sub> and TiO<sub>3</sub> is used to improve the thermal efficiency of the brake and to reduce CO

emissions [19].

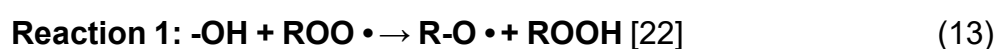
Fuel stability is one of the important criteria to decide the quality of the fuel. Several processes like oxidation due to aerobic environments, thermal decomposition due to excess heat, contamination due to presence of various impurities and high moisture contents can affect the fuel qualities in a significant way [20]. It is observed when fuels are stored for long term durations, fuel starts oxidizing by reacting with atmospheric oxygen leading to degradation of the fuel characteristics. The resistance of the fuel to react with oxygen especially during the long-term storage condition is called Oxidation stability. The additives which are used to overcome these stability problems in fuels are called stabilizers/antioxidants.

Due to the oxidation of the fuels, there will be change in the properties of the fuel like acid value, water content and peroxide value. All these properties value will increase due to the oxidation. As explained in the previous part of this chapter, Since the by-products that are formed in the autooxidation reaction includes, water, acid and peroxides [16] [17] etc. Therefore, all these values will be increased as intermediary products of the oxidation process.

The two main categories of antioxidants are phenolic and amines [20] where phenolic types are excellent hydrogen donors [21]. Some of the antioxidants used in the market are butylated hydroquinone (BHT), 4-allyl-2,6-dimethoxyphenol, tert-butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), propyl gallate (PG) and pyrogallol (PY) and etc [20].

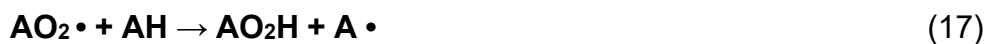
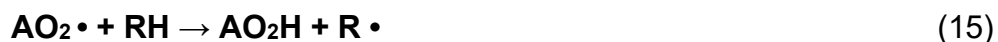
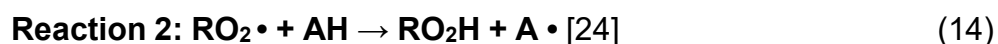
## 2.2.1 Chemistry of Antioxidants:

Antioxidants usually has one aromatic ring containing minimum one (-OH) hydroxyl group. From this active hydroxyl group of the antioxidant, hydrogen is abstracted by donating it to the hydroxyl radicals formed due to oxidation in fuels. This will neutralize the hydroxyl radical by forming quinone like structure of the antioxidant which is more stable than the radicals [22], [23].



The antioxidant reaction mechanism can also happen before the beginning of termination reaction when propagation reaction products are formed ( $\text{RO}_2 \bullet$ ) as shown

in below set of chemical reactions (14-18) [24].



Since,  $\text{RO}_2$  is a peroxide radical which will decompose further in termination reaction by reacting again with alkyl radical. During this stage, the antioxidant (AH) reacts with peroxide radical and leads to formation of hydroperoxide ( $\text{ROOH}$  or  $\text{RO}_2\text{H}$ ) and antioxidant radical  $\text{A}\cdot$  as shown in the reaction (14). This antioxidant radical will further react with dissolved oxygen in the fuel leading to the formation of further products. In the above reactions we can again see that (AH) antioxidant act as a barrier for the peroxide radical to further react and form products like acids, aldehydes and ketones. (AH) antioxidant donates hydrogen to peroxide radical, where it neutralizes the peroxide forming  $\text{A}\cdot$  which will further react with oxygen leading to formation of stable products ( $\text{AO}_2$ ) as shown on reactions (14) and (16) [24].

## 2.3 Accelerated Ageing

Accelerated ageing methods are used to forecast the behaviour of the liquid fuels in shorter time period when fuels are subjected to long term storage.

The primary purpose of the fuels is to store the energy and use it when necessary. The fuel should be stable and feasible for the storage and transportation. But, in recent years the major focus is on alternative fuels. Fossil fuels are non-renewable which will eventually deplete and be expensive in the future. Also, using fossil fuels involves damaging the environment with the pollutants and GHG's. This can be prevented by the usage of non-depletive resources and alternative fuels. Likewise, there are lot of research going on in the development of alternative fuels like oxymethylene ether (OME), methanol to gasoline (MTG) and several other alcohol blends with diesel etc. Therefore, it is very necessary to also know the behaviour of these alternative fuels during its long-term storage [4] along with conventional fuels. Instead of waiting for the fuel to age in normal conditions which takes several months and years, methods like

petroOxy, rancimat and bigOxy can be used to test the quality of the fuels. PetroOxy and rancimat are analytical methods used to determine the oxidation stability of the fuels. BigOxy is an accelerated ageing method which can age the fuels and predict their behaviour earlier in the matter of hours.

The ageing or degradation of the fuels lead to the formation of deposits or sediments in the bottom of the storage tank in the form of heavy molecular compounds. These heavy molecular formations can lead to the blockage of the fuel injectors and fuel lines, irregularities in the spraying of the fuels which make the fuel unfit to further use [4].

Practically, we don't have any methods to completely stop the auto-oxidation that occurs during the long-term storage of the fuels but, there is another way to control or slow down the ageing of fuels, which is by adding fuel stabilizers. As discussed earlier, there are different types of stabilizers which are mixed in the fuel to increase the stability of the fuels by resisting the ageing process. There is also ongoing research for the implementation of additives for novel fuels like gas to liquid (GTL), hydrotreated vegetable oil (HVO), e-fuels like oxymethylene ether (OME), alcohol blends etc [3].

## **2.4 The BigOxy Test Bench**

This is a modern accelerated ageing method developed by Tec4Fuels. This method enables us to test the long-term storage oxidation stability behaviour of the fuels like diesel, biodiesel (Fatty acid methyl ester-FAME), gasoline fuels, cooling fluids and lubricants. This method was used to perform all the experiments as a part of this thesis. In BigOxy we can also study the effect of the immersion of the materials (system components) in the fuel during the ageing test run. This enables us to study the compatibility of the different material components which are in the system that can be in contact with the fuel during various operating conditions [4]. The main advantage in the BigOxy method is that we can test the samples in larger volumes compared to other test methods.

The principle behind the BigOxy is derived from the petroOxy test method which is standardized with the engineering ISO standard DIN EN 16091. The difference is that the petroOxy is an analytical method which is used to determine the oxidation stability of the fuels. But the quantity of fuel used in petroOxy is very less (5 ml) compared to the BigOxy method. The BigOxy method can age up to 750 ml of the fuel, except the principle of subjecting the sample to higher temperatures to induce auto-oxidation reaction is same for both the methods.

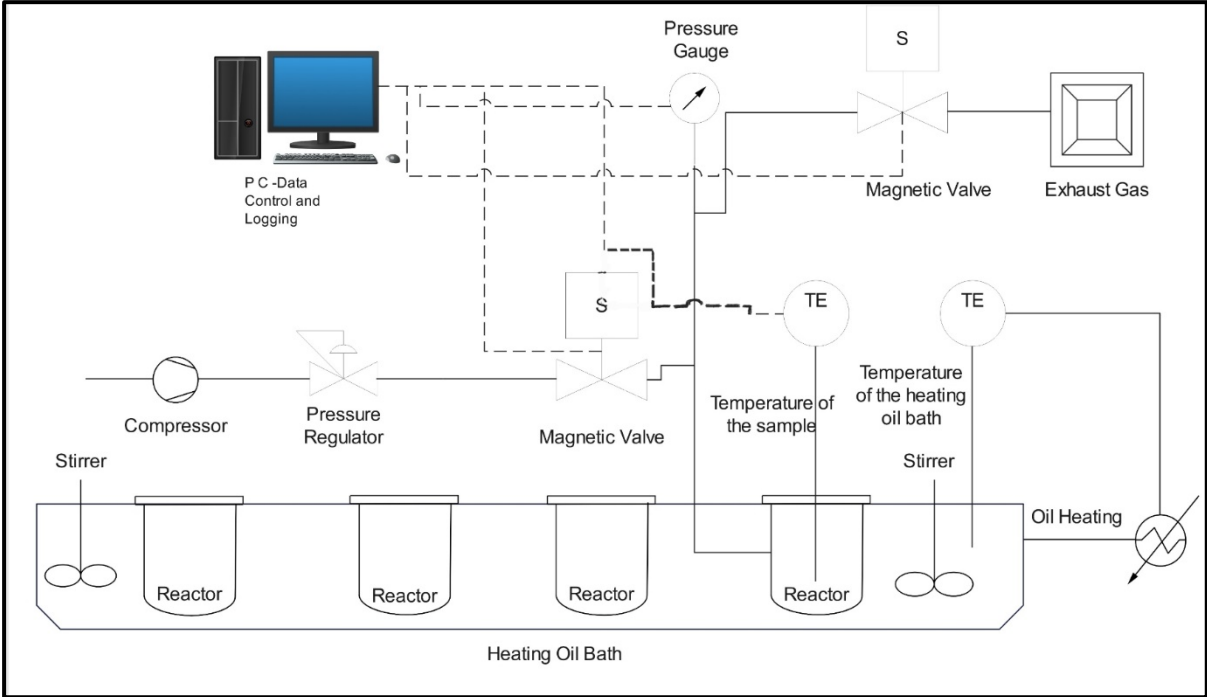


Figure 1 Piping and instrumentation diagram of BigOxy test bench

In the Figure 1, the P&ID (Piping and instrumentation diagram) of the BigOxy test bench is shown. It consists of a big hot oil bath and the reactors are placed inside the thermal bath setup to heat the fuel in the reactors and induce ageing. The test bench in Tec4fuels can accommodate up to 8 reactors for each test run. The thermal bath is heated by using a heat pump which is pre-set to certain set point based on the requirement for fuel temperature regulation.



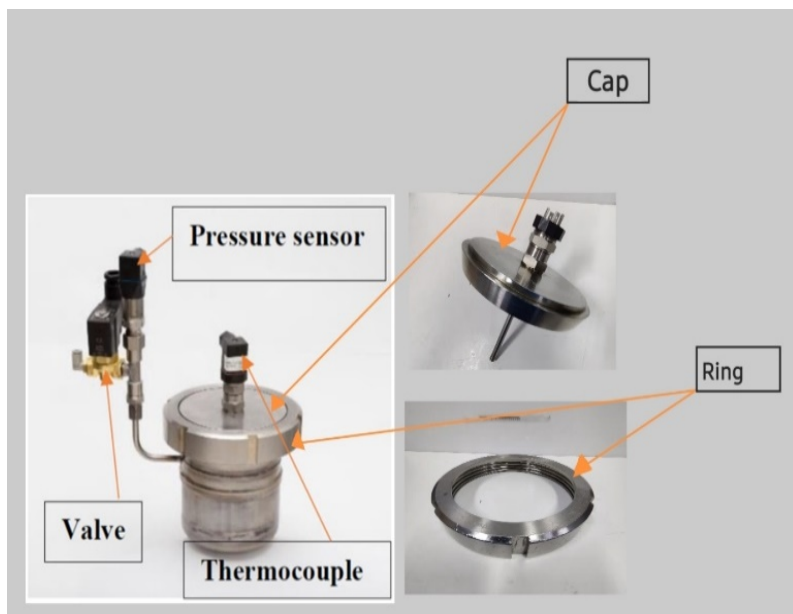


Figure 3 Components of BigOxy reactor

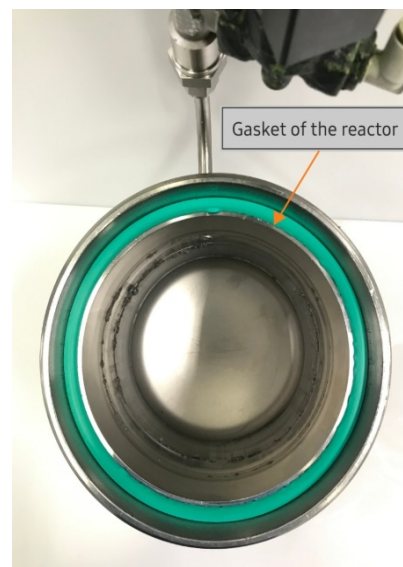


Figure 2 Interior of the BigOxy reactor

The Figure 3 shows the BigOxy stainless-steel reactor which has maximum volume of up to 1.5 litre and is retrofitted with a stainless-steel tube to its side. This tube has electrical components that is mounted to it. The cap of the reactor has PT 100 thermocouple which measures the temperature of the fluid inside the reactor. The stainless-steel tube side mount has a solenoid valve which regulates the gas flow (Air, nitrogen, and oxygen) in the reactor, and it has a pressure transducer which can measure the gas phase reactor pressure.

The pressure setting and the type of the fluid used can be changed for every reactor. Except, the heating bath temperature remains the same for all the reactors due to the presence of the one common heating oil bath. For each experiment the reactor can accommodate the fluid volume of up to 500 ml–750 ml. In this thesis experiments, the ideal volume of the fuel used is 500 ml for every reactor. The gas phase inside the reactors (oxygen required for auto-oxidation) can be induced with the pressure range of 1.2 bar – 5 bar and it is decided based on the requirements. The temperature of the oil bath after heating will be 101°C where the fluid temperature inside the reactor corresponds nearly to 95°C. The fluid temperature selection is based on the type of the fuel and requirements for testing. The heating oil bath can be heated up to maximum of 180°C.

The reactors are thoroughly cleaned using solvent like acetone to remove the traces and remains of the old fuel samples before filling the new sample and starting the experiment. The reactor is closed tightly after filling them with new fuel sample that needs to be tested. Then reactors will be pressurized with compressed gas (Air, nitrogen, and oxygen) based on the required pressure condition through the pressure valve. Aftermath the reactors are tested for pressure leakage for like 5 to 10 hours maximum and then if there is no leakage observed, the reactors are inserted in the heated oil bath. The experimental duration is flexible which depends and varies on the aim of the experiment, it maybe for 24, 48, 72 or 128 hours etc. The temperature and pressure data with respect to the time is examined and the aged fuel sample are used for the further chemical laboratory analysis.

### **2.4.1 BigOxy Experimental Procedure:**

The cleaning and preparation of the reactors is the primary and most important thing involved in experimental setup. Meanwhile during cleaning process, the heat pump is switched on, which enables the heating of the thermal oil bath to the set point temperature. The set point temperature that is used in all of thesis experiments is 101°C-102°C. This also depends on the outside weather conditions. The heating of the oil bath takes around 40-50 min to reach our set point temperature. Therefore, it is switched on parallely when cleaning and preparing fuel samples in order to save time.

The reactors are placed on the table and cleaned thoroughly with solvent like acetone by using cleaning paper. This involves cleaning the interior (bottom and sides) and cap of the reactor which will be in contact with fuel. There will be a gasket which is placed around the reactor top as shown in the Figure 2, it is made from FKM rubber material which is resistant to chemicals and higher temperatures. It is important to even clean that gasket before using. After cleaning with the acetone, the interior of the reactor and the cap are dried by pressurized air by use of an air gun. This is to make sure that the surfaces that will be in contact with the fuel during the experiment is clean and dry without any traces of acetone or any other dust particles. The cleaning is very important because, dust particles, and traces of fuel samples from the old experiments can cause variations in the results.

After cleaning of the reactors that is being used in the experiment, the second step is to fill the reactors with the fuel that we intend to test. The fuel is measured in the

cylindrical measuring tube and then poured inside the reactor. Before this, the measuring cylinder is cleaned with acetone and then rinsed with the fuel that is being used in the current experiment to get rid of the stains of the acetone and other unwanted traces of older fuels. Then 500 ml of the fuel is measured and filled inside the reactor. After filling the fuels in all the reactors, they are closed with caps and then tightened with hinged hook spanner with the help of hammer.

After all the reactors are closed and sealed. Then reactors are placed inside on the top of the test bench and then plugged in with all the three electrical components as shown in Figure 3. The pressure sensor which measures the gas phase pressure inside reactor, pressure valve which regulates the gas flow inside the reactor and thermocouple on the top of the reactor which measures temperature inside the reactor. The gas phase in the reactor is induced with the 5 bar pressure through pressure valve. The reactors are tested for pressure leakage for 5 h minimum, if there is any pressure leakage detected, the cap is removed and retightened. It is very important to maintain the constant pressure inside the reactor throughout the experiment to observe the auto-oxidation reaction inside the reactor. After the reactors are completely ready to be kept inside the heating oil bath, the thermostat of the heat pump is checked if the heating oil temperature is reached to the set point (101°C-102°C). If the set point temperature is reached, the reactors are kept inside the oil bath and doors of the test bench are closed which means that the experiment has started. The time duration of the experiment depends on the aim of the experiment and fuels used. In this thesis the experiments are performed for 24 h, 48 h and 72 h.

The temperature and pressure are monitored using the software called Siemens Logo. It is an uncomplicated user-friendly software with an intelligent logic module very suitable for automation and projects [25]. The real time pressure and temperature data is extracted through a software called Grafana. Grafana is a visualizing tool with a dashboard consisting various graph options which enables us to see, understand and extract data [26]. Likewise, it has all the information about the each and every experiment conducted in BigOxy including date, time, temperature and pressure conditions.

## **2.4.2 Data Analysis:**

The monitoring of the real time temperature and pressure occurs throughout the

experiment period. In the Figure 4 and Figure 5 shows the pressure and temperature curves obtained respectively from the BigOxy experiment which is plotted as the function of time.

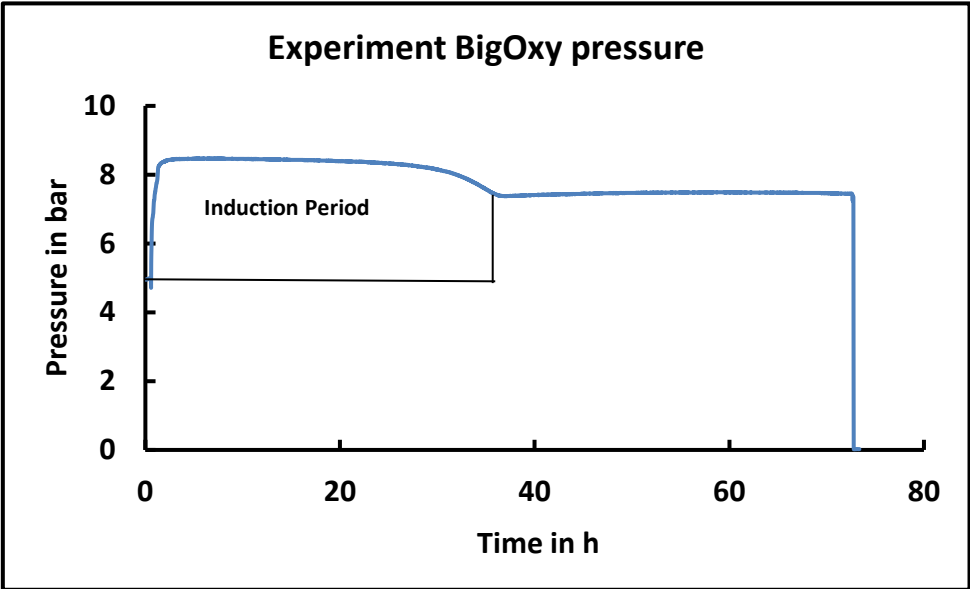


Figure 4 Pressure curve of the BigOxy experiment

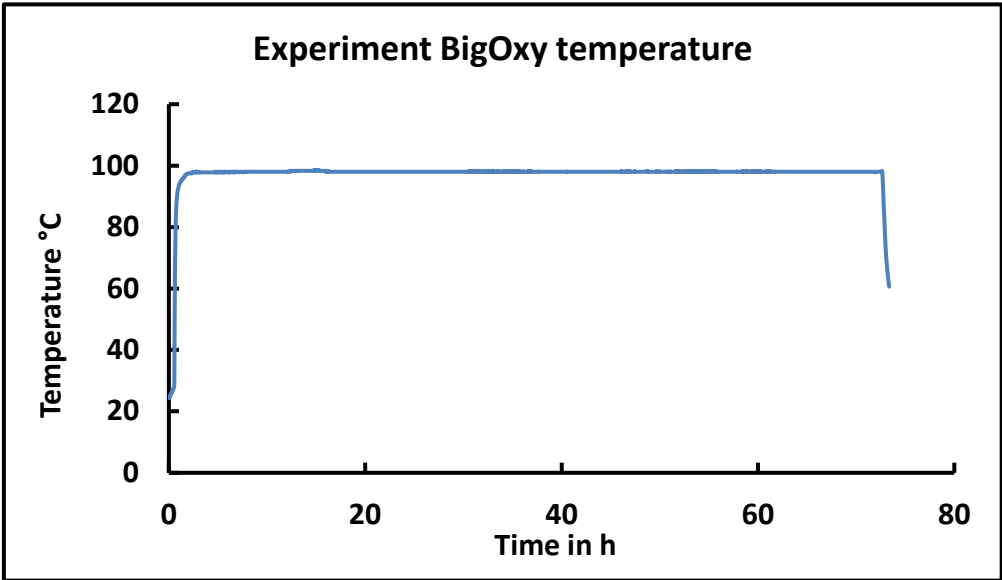


Figure 5 Temperature Curve of the BigOxy experiment

Figure 4 represents the pressure plot profile during the gas phase of the experiment and Figure 5 represents the temperature plot profile for the fluid which is inside the

reactor. Until the fluid resists to react with the reactor gas phase (atmospheric air), the pressure remains constant. When the fluid consumes the gaseous oxygen inside the reactor, the pressure will drop inside the reactor. The time interval between the start of the experiment (when reactors are inside hot oil bath) until the pressure drop is observed inside the reactor is referred to as the Induction period [4]. If there is no more free molecules of the fuel left to react with oxygen or vice versa, means the autooxidation has ended resulting in the pressure drop inside the reactor [4].

### **2.4.3 Fluid Analysis:**

After the samples are aged through BigOxy method, they should be tested in the chemical laboratory to check how effective our ageing method was. This is to study the changes in physio chemical properties due to the ageing. After ageing, the chemical composition of the fuel changes leading to formation of new products. The oxidation stability of the fluid is lost leading to the formation of acid, aldehydes, ketones and water molecules [4]. Usually, the analysis of the sample is done before (fresh samples) and after the ageing (aged samples) experiment to see the extent of change in their properties by comparing them [4]. There are some analytical tests like acid content (DIN EN 141 04), water content (DIN EN ISO 12937) and oxidation stability analysis (DIN EN 16091 and DIN EN 15751) like petroOxy which are performed to the samples after accelerated ageing. The critical properties like vapor pressure, density and viscosity can also be tested for fluids like coolants etc. By performing all these tests, it also provides a scope to check the efficiency of the stabilizers, property improvers which are additives. By categorization of the fluids with respect to its efficient additives enables us to prescribe the suitable fluid samples which can be feasible for respective operations.

### **2.4.4 Compatibility and Reproducibility:**

The compatibility of the test bench with the fluid is very important and this is tested by the observing the behaviour of fluid with the system components. The interaction of the fluid with the components like pump, pipes and other parts can be checked. All the components in the test bench that are in contact with the fluid is made of stainless steel and are corrosion resistant. Also, the oil specified heat pump is used for thermal oil in the test bench and the oil is changed for every 6 months. Because, as it is also a fluid

with heat transfer properties, it deteriorates due to constant high temperature conditions leading to an unpleasant smell. All the reactors in the test bench are made of stainless steel and hence there will be no interactions with the fluid. All the electrical components like transducers, thermocouple along with the valves are all resistant to the fluid interactions. Therefore, we can technically say that there will be no variation in results due to interactions of the components with the testing samples.

Along with the compatibility check, it is also very crucial to check the accuracy of the results that we obtain in the BigOxy test bench. The more we get the same results pattern when tested for multiple times with the same fuel sample, then it can be stated that the method is efficient and can reproduce the same results which makes it accurate. But, to reproduce the results there are some standard test procedures we need to follow. The fluid quantity should be measured by using the standard measuring cylinder before pouring into the reactor. The pressure regulators should be calibrated and ensured that there is no leakage which enables smooth functioning of the gas phase in the specified pressure conditions. The accuracy of the pressure transducer is around 0.5% with respect to the nominal value and the maximum deviation of the thermocouple sensor is 1 °C. The heating range accuracy of the hot oil bath is in the range of around  $\pm 1$  °C.

### **2.4.5 Applications of BigOxy:**

There is a wide scope for accelerated ageing methods in industrial research projects. This opens a huge platform to differentiate, study the stability behaviours of fossil fuels (gasoline, diesel) biofuels and e-fuels with blends of diesel and gasoline. The methodology of accelerated ageing is used to differentiate between the stability behaviours of the above-mentioned types of fuels. One more important application is that this can be used to test the feasibility of the stabilizers and behaviours of the stabilizers and additives with different fuel types. BigOxy offers the flexibility to test not only fuels but also cooling and lubrication fluids, to study their long-term behaviour for high temperature conditions. The parameters and testing conditions vary in accordance with the objectives, fuel types and customer's requirements but the method remains standard.

## 2.5 The PetroOxy Method

The PetroOxy is an analytical, rapid and small-scale oxidation stability testing method for fuels like gasoline, diesel, biodiesel, fatty acid methyl esters (FAME) blends, grease, cooling, and lubricating oils. This method is fast, safer and user friendly. The quantity of fuels used in this method to test the oxidation and long-term storage stability is very less compared to our BigOxy method. Basically, it uses small volumes and gives quick results. There are a many standards like ASTM D 525 - IP 40 – ISO 7536, ASTM D 2274, ISO 12 205, ASTM D 5304, ASTM D 7525, ASTM D 7545 – EN 16 0901, IP 595 etc., to perform the test [5]. The procedures involved in the test method varies slightly for different standards, but the aim of the experiment remains the same. For an instance ASTM D525 to test the influence of the antioxidants on raw gasoline with 40% olefin where the results are much faster. The concentrations of the antioxidant used also varies, ASTM D4814 test which uses 4 ppm of antioxidant, while EN 228 uses 30 ppm to fulfil the specification required for the test. The use of the much larger concentrations is not cost effective so there are certain standards that are followed which are established by predetermining the correlation between the concentration of antioxidant and the induction time [27] .

### 2.5.1 Test procedure and apparatus:



Figure 6 The PetroOxy apparatus

The commonly used petroOxy method is ASTM D7525 where 5 ml of the sample is loaded in the test cell, and it is closed by the lid. The test cell is then filled with the pressure of oxygen automatically and heats up to the standardized temperature of nearly 140°C. Then the pressure drop is continuously monitored until it decreases by 10% to the  $P_{\max}$  and this time interval is the induction period of the fuel [5]. As seen in the Figure 6, the petroOxy apparatus consists of safety and isolation hood, which is temperature stable. It has a real time digital display of the pressure and temperature curves for the sample inside. It has oxygen connection which automatically charges and discharges the pressure up to 8 bar. It mainly has a test cell which is chemically stable/inert and is gold/stainless steel/aluminium plated. The test cell can accommodate maximum 5 ml of the sample, very easy to clean and is automatically re-cooled. The test duration is approximately less than 1 hour even for the new users and it hardly takes 5 minutes for cleaning and handling the apparatus after every experiment [5].

### **2.5.2 Applications and advantages:**

Along with the liquid fuels like gasoline, diesel, biodiesel, cooling and lubricating fluids, petroOxy method also provides a huge scope to measure the oxidation stability of the various food, cosmetics and other products. Products like vegetable oils, animal oils and fats, meltable foods like cheese and butter and cosmetics like lipstick can be tested to examine their shelf life in the petroOxy method as well [5].

The time required for the testing is very less along with the cleaning and setup time is maximum 5 mins in the automatic petroOxy method. The results can be reproduced and repeated in short time which makes it cost effective. This is a fast small scale ageing apparatus where the pressure drop can be seen on the digital screen easily. In case of accidents, the inspections can be done very fast and also routine monitoring is easy and quick. There is no need of preparing the sample for test and use of harmful chemicals for cleaning. It provides a complete analysis of the results for the samples which include all the volatile and non-volatile (heavy molecules) oxidation products. The cooling of the apparatus is very fast after every experiment which makes it less time consuming to start new test.



## 2.6 The Rancimat Method

Rancimat is an analytical oxidation stability testing method which can also be used as accelerated ageing test [6] method like petroOxy. There are many standards for the rancimat ageing method. This again depends on the type of the fuels used to determine the oxidation stability. Some of the standards are ASTM D 6571 for biodiesel fuel blends (B100), ASTM D 7467 for diesel fuel oil and biodiesel blends (B6 TO B20), EN 14214 for automotive fuels like diesel engine FAME, (Fatty acid methyl esters), EN 14213 for heating fuels of FAME, EN 14112 for fat and oil derivatives, EN 15751 for FAME fuel and diesel fuel blends and EN 590 for diesel automotives [28].

### 2.6.1 Test procedure and apparatus:



Figure 7 The Rancimat apparatus with measuring positions

In the Figure 7, shown the rancimat apparatus. Here the fuel sample of 20 ml [29] will be exposed to an airflow in a constant temperature in the range of 105°C - 120°C [29]. This initiates the oxidation in the fuel samples which is contained in the heated reaction vessel. Due to the oxidation of the sample with oxygen in the airflow, alkyl radicals are formed which leads to the formation of the peroxide molecules (Initiation reaction) which are the primary oxidation products. After some time, the oxidation reaction continues where the peroxide molecules decompose and leads to the formation of the alkoxy and hydroxyl radicals (propagation reaction). This results in the formation of alcohols, aldehydes, ketones etc., which are the secondary products of the oxidation. Now these secondary products are transferred into the second vessel which contains distilled water by the airstream [28]. Here the conductivity of the sample is monitored continuously until it is increased. This increase in the conductivity denotes that the

alkoxyl and hydroxyl molecule are decomposed (termination reaction) leading to the formation of the heavy molecules like alcohols, ketones, aldehydes, acids etc. This may further lead to the formation of the macromolecules like polymers which indicates that the oxidation reaction has come to an end. This indicates the oxygen is completely consumed in the reactor vessel. This time interval from the beginning of the test until the final secondary products are formed, which is seen as the increased conductivity in the sample is called induction period of the sample. As explained in the earlier methods, the induction periods characterize the oxidation stability of the fuel sample. The induction period of the for biodiesel is 8 hours minimum according to EN 14112 standard [30]. The results and stability measurements are analysed by using software tools.

### **2.6.2 Applications and advantages:**

The rancimat oxidation stability is very user friendly and in compliant with standards. The compiling of results is very quick and especially with the software tool for instrument control and evaluations. We can analyse simultaneously 8 samples together which is convenient and time saving. Each measuring position is independent of one another in terms of start time and heating. The temperature is independent for each heating blocks. Once the experiment starts, the measurements can be done individually after the sample is put in the position. Along, with the oxidation stability test for fluids like diesel, biodiesel (FAME) blends and gasoline, rancimat can also be used to conduct stability tests for products like oil, vegetable oils, animal fats and food products containing fats and oils such as instant noodles, cookies and nuts. It can also be used to test cosmetics consisting of oils and fats [6]. The effectiveness of antioxidant can also be studied by the application of rancimat for animal oils and fats.

## **2.7 Laboratory Analytics**

After the accelerated ageing of the liquid fuels, they should be subjected to analytical tests in laboratory. As discussed earlier, the physical and chemical properties of the fuel will be changed after the ageing. These properties include water content (WC), acid content (AC), density, viscosity etc. Hence, by testing these properties, an idea of how effective the ageing was can be obtained. The extent of property changes occurred in the aged fuel is studied by comparing the results of fresh samples. Some

of the important analytical test methods for these properties are discussed below.

## **2.7.1 Water Content:**

According to DIN EN ISO 12937 standard there is a specific method that is followed to find out the water content present in the fuel sample. The method is known as Karl Fischer titration which involves coulometric titration of the mineral oil samples (petroleum oils) which are below in the boiling point range of 390°C. This method can also be used for lubricating oils except for the oils which consists of ketone content [3].

### ***a. Test procedure and Principle:***

At first draw 3 ml of aged sample in the syringe and try to take out air bubbles. Then by using the analytical balance, weigh the sample. Approximately 1 ml of the sample is added through septum to the titration vessel [3]. Start the measurement by entering the weight of the sample injected to the titration vessel.

The sample that needs to be analysed for water content will be placed inside the titration vessel of the Karl Fischer coulometric apparatus which has an anode and a cathode. In the anode, iodine is formed coulometrically from the titration. Once all the water is consumed in the titration, the excess iodine is detected voltametrically with the electromagnetic end point detector which is the indicator electrode. There will be a signal in the detector which means the titration has come to an end. Based on the stoichiometric reaction, 1 mol of iodine reacts with 1 mol of water [3]. The quantity of water is calculated with respect to the iodine concentration in Karl Fischer titrating reagent and also with quantity of Karl Fischer reagent consumed during the titration. Therefore, the amount of water content is proportional to the total electric current consumed which is based on Faraday's law.

## **2.7.2 Acid Content:**

Acid content is the measurement of acidity. It is determined by the amount of potassium hydroxide (mg), which is a strong base, required to neutralize the free acid content in 1 mg of fuel. It is also the measure of potassium hydroxide (mg) that is required to neutralize the free fatty acid contained in unit mass (g) of chemical substance [3].

### ***a. Test procedure and Principle:***

The acid content test is conducted generally according to the DIN EN 14104 standard. This is also based on the neutralization titration. In the 150 ml glass beaker 20 g of sample is filled. Then the accurate weight of the sample is noted down. Then 50 ml of diethyl ether, 300 µl of phenolphthalein which acts an indicator and 50 ml of the ethanol is mixed with the 20 g of the fuel sample. The quantity of strong base like KOH solution is mixed with the acid solution (fuel sample, diethyl ether, ethanol, and phenolphthalein). The measuring device gives us how much KOH is needed to neutralize the acidic content in our solution when we keep our acidic solution in the beaker on it. By measuring the volume of the acidic solution, the device gives us vol (ml) of KOH that needs to be used. Finally, all the mixtures are added to the electrode stirrer set up and process starts.

The acid value is calculated using the equation (19) [17]:

$$X = 56.1 \times N \times V/G \quad (19)$$

Where, X – acid value in the oil sample (mg KOH/g)

N – Concentration of the Potassium hydroxide (KOH) ethanol solution (mol/l)

V – Volume of KOH ethanol solution consumed during titration (ml)

G – Mass of the sample (g).

### **2.7.3 Oxidation Stability:**

The Oxygen stability test is used to find out the consumption of the oxygen due to oxidation reaction. This is done by the determination of the partial pressure of the oxygen with respect to the time at defined temperature of the fuel. A 10% pressure drop in the gas phase (reaction of O<sub>2</sub> with the fuel) to the maximum pressure is considered as abort criterion.

### ***a. Test procedure and Principle:***

The fuel sample of 5 ml is placed in a small reactor, and this will be exposed to the pure oxygen in the atmospheric pressure range of 700 kPa in 140°C temperature. The temperature and pressure are continuously monitored [17]. In the heating phase, there will be increase in the pressure and it will reach up to 10 bar which is caused to the

expansion of the oxygen. Due to this thermo-oxidative degradation and auto-oxidation reactions which occurs between fuel and oxygen in high temperature, there will be a decrease in the pressure which indicates all the oxygen have been consumed or oxidized with the fuel. This time interval from beginning of the heating phase to decrease in the pressure drop determines the resistance of the fuel towards oxidation.

## **2.7.4 Density and Viscosity:**

There are certain standards that are followed to measure density and viscosity for the fluids. Some of them are, Density – EN ISO 12185, ASTM D4052, IP 365; Dynamic viscosity – ASTM D7042, Viscosity index – ISO 2909, ASTM D2270, Kinematic viscosity – ASTM D7402, EN 16896, DIN 54659 [31].

### ***a. Test procedure:***

The sample is first mixed thoroughly to its homogeneity and 3 ml of the sample is drawn through syringe. Inject the sample drawn gradually in the measuring cell and later after 5-6 hours, all the measured parameters like density, viscosity and viscosity related other parameters can be obtained. The device that is normally used to measure these parameters is called SVM 3001 Stabinger Viscometer [31].

# Chapter: 3

## Aim and Methodology

In this chapter the aim of the thesis is clearly discussed. We can observe the detailed research chronology and methodology involved to study the ageing behaviour of the liquid fuels like gasoline, methanol (e-fuel) and blend of methanol and gasoline. Discussed in the chapter are the main experimental method and test procedures which are particularly used in this thesis. As mentioned in the beginning, BigOxy method is used throughout this thesis work for accelerated ageing of fuels. The BigOxy aged samples will be analysed for the parameters involved and their influences on ageing. In this chapter, the comparison between BigOxy and other stability test methods, by considering common parameters involved in all the test methods are discussed. Discussed, the fuels used for the accelerated ageing in the BigOxy and along with the fuels used for analytical tests (PetroOxy, Acid and Water content) that were conducted.

## 3.1 BigOxy vs Rancimat and PetroOxy

The main objective of this thesis is to validate and standardize the BigOxy method of accelerated ageing for liquid fuels. Particularly fuels like gasoline, e-fuel like methanol and their blends will be tested for their oxidation stability by conducting multiple BigOxy experiments. The end results give us how efficient is the BigOxy method to study the ageing behaviour of the fuels used. The efficiency of this method is standardized by checking how repeatable the results are. This enables to analyze the rate of effects of parameters like pressure and temperature on the accelerated ageing of fuels for 24 h, 48 h, 72 h etc., durations inside the BigOxy reactor.

There are several oxidation stability analytical test methods available in the market as mentioned in the previous parts of this chapter. But, in this thesis only BigOxy accelerated ageing method is used. The reason of selecting the BigOxy method over others is, mainly due to its flexibility in the experimental procedure, and compatibility for obtaining repeatable results by varying the experimental parameters. More importantly in BigOxy larger volume of fuel samples can be used (up to 750 ml) which is not possible in any other methods. Using large volume of fuel samples for the tests makes it easier to analyse the long-term storage stability results more accurately, because fuels that are stored for many days are stored in larger quantities in storage tanks. Therefore, using larger quantities for experiments makes it more comparable to the actual long term storage conditions. The comparison between the three main oxidation stability tests (BigOxy, PetroOxy and Rancimat) based on the parameters used are given in the below table.

<b>Parameters</b>	<b>BigOxy</b>	<b>PetroOxy</b>	<b>Rancimat</b>
<b>Pressure</b>	<p>There is no standard pre-determined set point. It offers up to 12 bar maximum.</p> <p>Provides flexibility to test for various pressure conditions and to study the influence of pressure on ageing.</p>	<p>In PetroOxy the pressure is predetermined and already set to 7 bar [5]. This is a standard and cannot be varied or changed. The pressure is pre-programmed.</p>	<p>In Rancimat it is not possible to study the influence of pressure at all. Because here no pressure is involved. Only the flow rates of airstream are involved.</p>
<b>Temperature</b>	<p>In BigOxy test bench, the allowable temperature is up to 180°C-200°C maximum. But, for the thesis experiments with gasoline and methanol, 100°C - 102°C was sufficient.</p>	<p>In PetroOxy the temperature is also pre-programmed like pressure. The temperature is set to 140°C for diesel and gasoline [5]. There is no flexibility to test in various temperature range.</p>	<p>In Rancimat the standard test temperature used for diesel and biodiesel is 120°C. But it offers maximum temperature range of up to 50°C - 220°C [6].</p>
<b>Volume</b>	<p>The BigOxy reactors can accommodate the volume of up to 750 ml of fuel in it. 500ml of fuel samples are used in this thesis to test in the experiments.</p>	<p>The volume allowance in PetroOxy is very less and is fixed which is 5 ml for each experiment [5].</p>	<p>In Rancimat the allowable volume of fuel sample to test is 20 ml [28]. It is standard volume to test diesel and biodiesel blends.</p>



<p><b>Experiment Duration and Set up time</b></p>	<p>In BigOxy test bench, the experiment can be run as long as needed. In this thesis the experiment durations used are 24 h, 48 h and 72 h. The experimental set up for BigOxy takes 1 h-2 h.</p>	<p>In PetroOxy the test run duration and obtaining of the results will be approximately less than 1 hour. The cleaning and setting up the apparatus take maximum 5 minutes.</p>	<p>The experiment duration of rancimat for diesel, biodiesel and blends is 3 h – 8 h [30]. Since disposable glass parts are used, this doesn't require much time for cleaning and setting up of the experiment.</p>
<p><b>Fuels Used</b></p>	<p>Fuels like gasoline, diesel, biodiesel (FAME), methanol can be tested. Fluids like heating oils, lubricants and many more liquids can be tested in BigOxy.</p>	<p>Fuels like gasoline, diesel, biodiesel (FAME) and fluids like grease and oil can be tested in petroOxy.</p>	<p>Fuels like diesel, biodiesel (FAME) and their blends can be tested in rancimat.</p>

Table 1 Comparison of BigOxy with PetroOxy and Rancimat methods

As the above comparison in Table 1 validates the advantages of using the BigOxy method over the other two oxidation stability methods in terms of fuel volumes, flexibility in parameters (pressure and temperature) and compatibility of fuel types. Therefore, all the experiments that are conducted in this thesis regarding to accelerated ageing of fuels are performed by BigOxy method. All the results that are given in this report for accelerated ageing are the BigOxy experimental results. Along with this the laboratory analytical results are also discussed. There are different analytical methods for different requirements like oxidation stability, water content, acid content, density, viscosity etc., out of which some of the results are also discussed.

The main laboratory analytical methods that are used in this thesis are water content and acid content, the petroOxy oxidation stability tests were also performed for the fresh samples and BigOxy aged fuel samples (24 h, 48 h and 72 h). These results are compared and analysed.

## **3.2 Fuels used for experiments and analysis**

### **3.2.1 Gasoline, Pure methanol (M100) and Blend of Gasoline with Methanol (M15):**

In this section, the types of fuels are used to test in BigOxy test bench and to study their ageing behaviour with respect to long term storage are discussed.

Two types of gasoline with different qualities (manufactured at different times) are used, and they are named as Gasoline A and B. Gasoline, which is known as petrol, is an energy dense secondary fuel which is obtained from fractional distillation of crude oil. It is a fossil fuel which is used to power heat and IC engines and to run IC engine cars and vehicles. The hydrocarbon chains of gasoline constitute aromatics, olefins and saturates. It consists 4-12 molecular chains of carbon atoms [32]. Therefore, two types of gasolines are used to establish a comparative standard for accelerated ageing in BigOxy with respect to gasoline. This is because, not all the gasolines in the market have the same stability for long term storage and it depends on their quality. The quality is not always same for the gasoline, and it varies every time. Gasoline is a middle distillate fuel (refined product obtained from crude oil separation through fractional distillation) where it comes in the lighter product side along with LPG [33]. The main reason for variation in the quality among different gasolines is because gasoline is not a pure molecule, and it is a mixture of several hundreds of hydrocarbons, cycloalkanes, alkenes and alkanes [33]. The quality of these constituent mixtures varies with respect to their extraction temperatures. Initially during the crude oil extraction, the temperature of the crude oil will be around 65°C-150°C [34] and this temperature varies according to the geothermal gradient temperature during its extraction. Along with this there are several other factors like cooling which occurs as the fluid rises up in the bore from the reservoir, and in refineries, gasoline is also treated with additives/stabilizers before catering it to the market.

Hence, two types of gasolines are used to set a comparative standard by checking the repeatability of results for both by conducting multiple tests in BigOxy. By doing this it will be very convenient to compare the e-fuel like methanol that we are using with both

gasolines A and B, and can also compare gasoline methanol blends with pure gasolines A and B. To establish a strong comparison between e-fuel, gasoline and their blends, we need to have a BigOxy standard (induction period) that is set for them individually. Similarly, in this thesis for pure gasoline, it is achieved by testing for two types of gasolines (A and B).

After gasoline, the second fuel that is used in this thesis is M100 which is pure liquid methanol. Here there is no need to use two types of methanol because methanol is a pure molecule and not a mixture of different molecules like gasoline [15]. Therefore, the methanol quality remains almost same, and the effects are negligible. As discussed earlier in the chapter 1, the methanol that is used in all the experiments of this thesis is an e-fuel.

The third type of fuel that is used is a blend of Gasoline+Methanol. Since 500ml of fuel is tested in each reactor for every experiment. M15 consists of 15% methanol that is 75 ml and 85% of gasoline which is 425 ml. Since two types of gasolines are used, both M15 gasoline A and M15 gasoline B blends are used to test in the BigOxy experiments. As discussed in the chapter 1, the scope of methanol and mixing it with gasoline to run the IC engines, therefore it is essential to test the ageing behaviour for this blend to check their long-term storage stability.

Hence, standardization of the BigOxy test method is done for gasoline (A and B), liquid Methanol (M100) and their M15 blends (M15 Gasoline A and M15 Gasoline B) with respect to their induction periods. One of the main aims of this thesis is to study the ageing behaviour of these fuels by achieving the repeatability of the results that we obtain from BigOxy. By doing this, BigOxy ageing standards for all three fuels with respect to their induction periods can be determined. Since, BigOxy method is a custom-built test bench which is developed by Tec4Fuels, and It is not commercialized in the market and neither in compliant with any engineering standards. It is very important to set standard induction times for the fuels used with respect to their ageing behaviour.

### **3.2.2 Fresh fuel samples:**

Since, the accelerated ageing in BigOxy method and parameters involved are being analyzed. We need to have a standard comparison to compare the BigOxy aged samples to know the effect of our experimental analysis (efficiency). This was achieved by using the fresh fuel samples (M100, M15 Gasoline A, M15 Gasoline B, Gasoline A

and Gasoline B). All the BigOxy aged samples were compared with their respective fresh samples to understand how these fuels behave during long term storage with respect to the rate of changes (degradation) with respect to oxidation stability.

### **3.3 Methodology and Approach**

As discussed before, the main objective of this thesis is standardization of the BigOxy accelerated ageing method for the fuels like gasoline, e-fuel like methanol and for their blends. This involves studying their ageing characteristics and categorize the results with the specific fuel types (Gasoline A, Gasoline B, M100, M15 Gasoline A and M15 Gasoline B) and to their respective induction periods. After this, the BigOxy method is validated by conducting laboratory analytics (PetroOxy, water and acid contents).

Since BigOxy is a new method, it is very essential to establish the standard induction periods for the fuels that are being used. The scientific way to do it is checking how repeatable the results are for a specific fuel with respect to their ageing durations. For an instance if we have aged gasoline A for 24 h in BigOxy, if the pressure drop duration (induction period) is around 18 h. Then we cannot just validate that BigOxy is accurate for all 24 h tests for the gasoline A that was tested. It is very important to repeat the same test for same gasoline A with the same previous test conditions. Then if the induction period is again approximately 18 h, it can be stated that the standard induction period for gasoline A in BigOxy will be nearly or equal to 18 h. Likewise, in this thesis the same research approach is followed to test all the fuels that are used.

The fuels were standardized in BigOxy with respect to three times frames of experimental durations which are 24 h, 48 h and 72 h. We can do it for more period like 96 h and 120 h etc., if you need it, which depends on the oxidation stability of the fuels. In this thesis the main focus is for these three-time frames where fuels are aged in the BigOxy test bench. Multiple experiments of 24 h, 48 h and 72 h experiments have been conducted for all the three fuels to check how repeatable the results are, the repeatability was checked with respect to the pressure drop durations and then repeatable results are filtered out. The samples of these experiments which showed repeatability are analysed for water content, acid value and PetroOxy.

As mentioned earlier we need a standard comparison to validate the efficiency of BigOxy method that we are using. Therefore, the BigOxy aged samples are compared with fresh

samples. The comparison is done by using the results of analytical methods (PetroOxy, Water content and Acid value) for both fresh samples and BigOxy aged samples. Comparing the BigOxy aged samples with fresh samples gives us a clear understanding on how efficient the BigOxy method is and how these fuels behave during long term storage in real life with respect to their oxidation stability. The result comparisons of acid value and water content for BigOxy and fresh samples depicts the rate of effectiveness of auto-oxidation in BigOxy. The water content and acid value for the BigOxy aged sample will be high because, as discussed earlier, water and acid are the products formed during auto-oxidation reaction. In the same way for petroOxy, results comparisons for the oxidation stability for BigOxy samples will be low compared to fresh samples. Therefore, these comparisons validate the efficacy of BigOxy method.

In the next chapter, the results of BigOxy ageing experiments conducted for fuels used in 24 h, 48 h and 72 h ageing are discussed. The results of water content, acid value and petroOxy tests conducted for BigOxy aged and fresh samples are discussed and compared.

# Chapter: 4

## Results and Discussions

Discussed in this chapter are the results that are obtained from BigOxy accelerated ageing experiments and results for the laboratory analytics for petroOxy, acid content and Water content. Results for all the fuel samples used (Gasoline A, Gasoline B, M100, M15 Gasoline A and M15 Gasoline B) are discussed. Detailed comparison for all the fuel samples with respect to their BigOxy experimental time frames (24 h, 48 h and 72 h) and with their laboratory analytical results are shown in this chapter. BigOxy results are represented with pressure curves showing induction periods. The analytical results comparison is shown with specific graphs as well. The comparison of BigOxy aged samples vs fresh samples is also discussed with analytics results. The oxygen consumption calculation for fuels during auto-oxidation reaction in BigOxy experiments are also discussed with the method of calculation.

### 3.4 Results for 24 h BigOxy Experiments

#### 3.4.1 Gasoline A:

The Figure 8 shows the pressure curves of the Gasoline A aged for 24 h in BigOxy test bench. Each curve in the graph represents the individual reactors used for the specific experiment. The x-axis represents time (h) and y-axis represents the normalized pressure values ( $P_{\text{actual}}/P_{\text{max}}$ ) in bar. Since many reactors are being used at the same time in one experiment, multiple pressure curves are obtained. Therefore, normalizing the pressure curves makes it easier to understand and compare the results. The normalizing is done by dividing the actual pressure values ( $P_{\text{actual}}$ ) for each minute by the max pressure value ( $P_{\text{max}}$ ) obtained for each reactor during a specific experiment.

In Figure 8 the pressure curve is shown for the 24 h experiment conducted for Gasoline A with 5 bar pressure and 95°C, it can be observed that the pressure is stable throughout the experiment duration (24 h). There is no pressure drop at any point of time for Gasoline A. Therefore, it can be stated that oxidation stability of Gasoline A is high for 24 h experiment. The absence of pressure drop indicates that the auto-oxidation reaction is absent due to the unavailability of alkyl radical. The Figure 8 shows two curves which represent two experiments, this also shows the repeatability of the BigOxy test method.

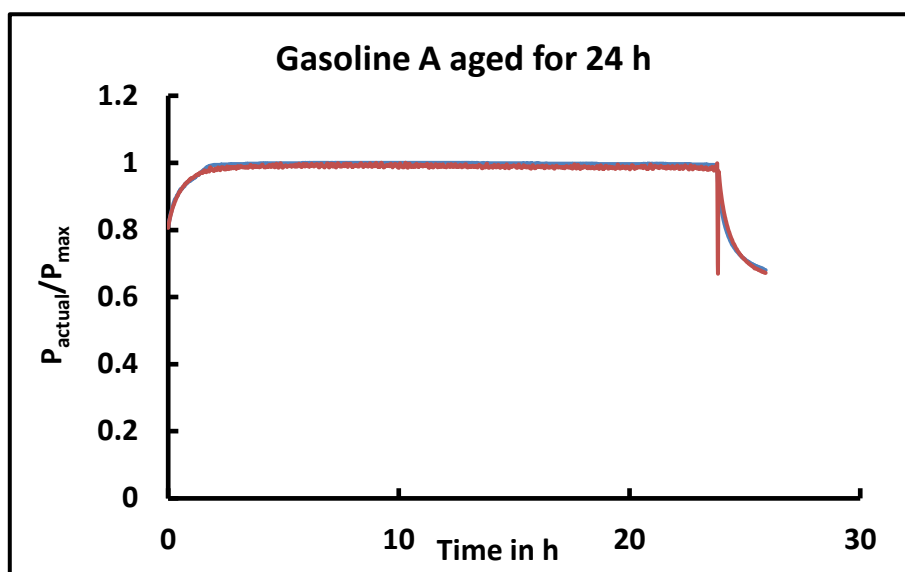


Figure 8 Gasoline A aged for 24 h in BigOxy method

### 3.4.2 Gasoline B:

Similarly the Figure 19 of the Anexe1, shows the pressure curves for the 24 h experiment conducted with 5 bar pressure and 95°C for Gasoline B. The behavior of the gasoline B is also similar to Gasoline A for 24 h experiment. There is no pressure drop, and the fuel is very stable throughout the experiment.

By analyzing and comparing the 24 h results for Gasoline A and Gasoline B, it can be stated that they are stable for 24 h accelerated ageing BigOxy experiment. They need more induction time (>24 h) to start auto-oxidation by forming alkyl radical by breaking their bonds. Their bonding (C-H) energy is high ( $413 \text{ kJ mol}^{-1}$ ) [18], which means the resistance for oxidation is more. By looking at the graphs, it can be stated that the results for Gasoline A and B for 24 h experiment in BigOxy is repeatable and standardized

### 3.4.3 M 100:

In the Figure 9, the pressure curve for pure liquid methanol (M100) aged for 24 h with 5 bar and 95°C can be observed. The fuel is very stable and there is no pressure drop in the graph. It really makes sense for the absence of pressure drop. Because, gasoline being a mixture of several olefins and diolefins with unsaturated double bonds [32] is stable in 24 h experiment. Methanol being a pure molecule with saturated single bonds having only one methyl group linked to hydroxyl group, [35] definitely should make it more stable than gasoline in 24 h BigOxy experiment. Here it should be noted that, though there is no auto-oxidation reaction in the liquid phase, but there will probably be reaction of methanol with oxygen in the gas phase. Methanol vapours reacts with gaseous oxygen and can form formaldehyde (CH<sub>2</sub>O) and water [36] as shown in the below reaction (20). These products can later condense after the experiment is completed and reactor is cooled down. But this reaction does not affect the oxidation stability of liquid methanol in 24 h experiment as seen in Figure 9.

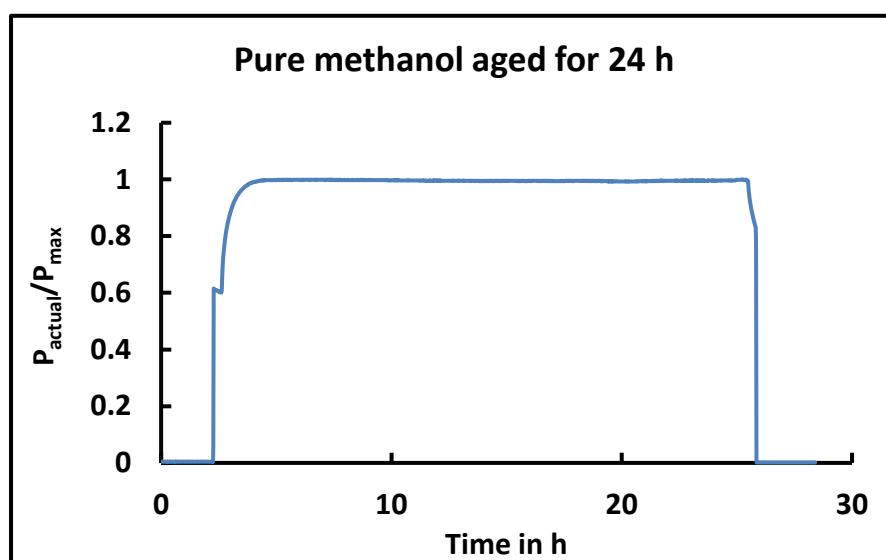


Figure 9 M100 aged for 24 h in BigOxy method

### 3.4.4 M15 Gasoline A:

The Figure 10 shows the pressure curves for the 24 h BigOxy experiment for M15 blend of Gasoline A. The curves are stable and not showing any auto-oxidation through pressure drop. Here it can be noted that gasoline being a non-polar molecule and



methanol being a polar molecule [37], Methanol is not 100% blended (homogenous) with gasoline. The solubility of the methanol molecules in gasoline is also very slightly less because of their different chemical structures. But here it can be stated that there is no formation of alkyl radical in 24 h BigOxy experiment of M15 gasoline A and the fuel needs more induction time (>24 h) to break the bonds and react with oxygen and is stable for 24 h BigOxy experiment.

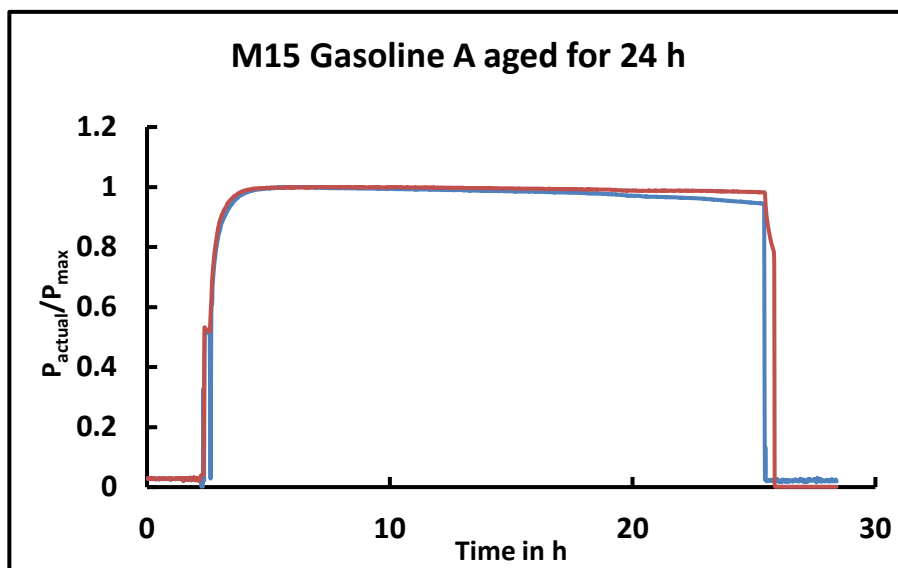


Figure 10 M15 Gasoline A aged for 24 h in BigOxy method

### 3.4.5 M15 Gasoline B:

From the graph shown in Figure 11, the pressure drop has begun from 12<sup>th</sup> hour approximately. This depicts that the auto-oxidation reaction has started after 12 h and the liquid fuel has started the reaction with the gaseous oxygen in the reactor. It can also be observed that the curve is almost stable after 23 h approximately after the pressure drop. This indicates that the oxygen in the reactor is consumed by the fuel by auto-oxidation reaction where the initiation and propagation reaction has ended resulting in the pressure drop.

The stable curve after the pressure drop (23 h) represents the final auto-oxidation phase which is termination reaction which involves formation of heavy molecular substances. In this experiment it can be stated that the induction period for M15 gasoline B is approximately 23 h for the BigOxy accelerated ageing method. Here it can be seen that

the oxidation stability has decreased slightly after adding methanol (15% vol) to gasoline B. The slight decrease in oxidation stability might be due to the additional unsaturated bonds (weak bonds) formed after blending methanol and gasoline B.

By comparing the results of M15 samples for gasoline A and B. It can be observed that the oxidation stability of M15 gasoline A is higher than M15 gasoline B. M15 gasoline B is almost showing pressure drop after 23 h.

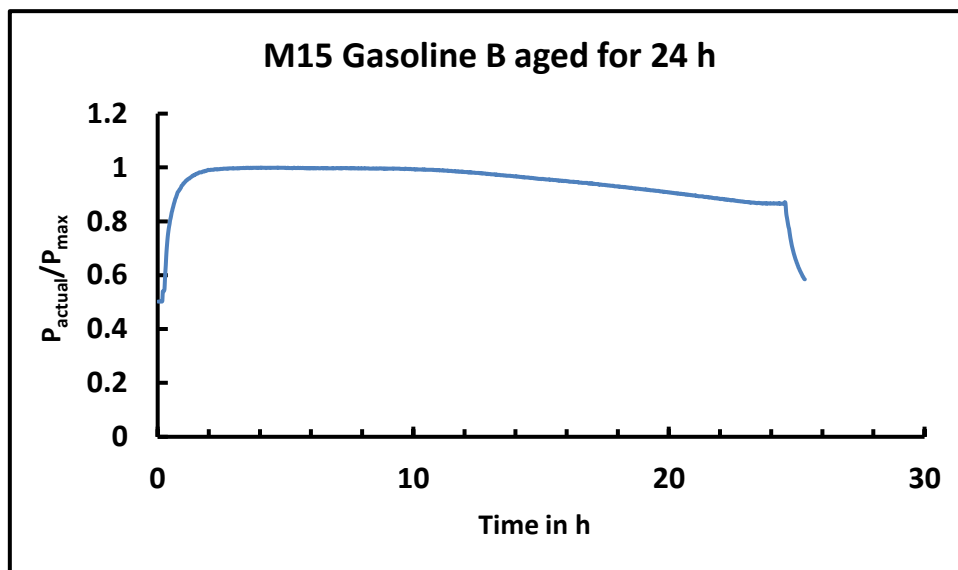


Figure 11 M15 Gasoline B aged for 24 h in BigOxy method

## 3.5 Results for 48 h BigOxy Experiments

### 3.5.1 Gasoline A:

From the graph in Figure 20 of the annexe 1, it shows the pressure curves for the 48 h ageing experiment of Gasoline A aged under 5 bar at 95°C. There is no pressure drop in the curves which indicates the fuel is stable and the oxidation stability is higher than 48 h. Here the fuel might need even more energy ( $>413 \text{ kJ mol}^{-1}$ ) to react with oxygen by breaking the bonds and to undergo auto-oxidation. It can also be observed the curves are repeatable. Therefore, the oxidation stability of gasoline A is higher for 48 h BigOxy accelerated ageing experiment.

### 3.5.2 Gasoline B:

Figure 12 represents the pressure curves for Gasoline B aged for 48 h under 5 bar at

95°C. Here the pressure drops for both the experiments conducted for 48 h can be observed. The pressure drop is observed after 24 h-26 h approximately. This indicates that the auto-oxidation reaction is completed and has reached its final termination stage after 24 h in the experiment. Here the oxidation stability of the gasoline B in BigOxy accelerated ageing method is approximately 25 h. Here the results are repeatable where the pressure drop for both the experiments are most likely matching with each other.

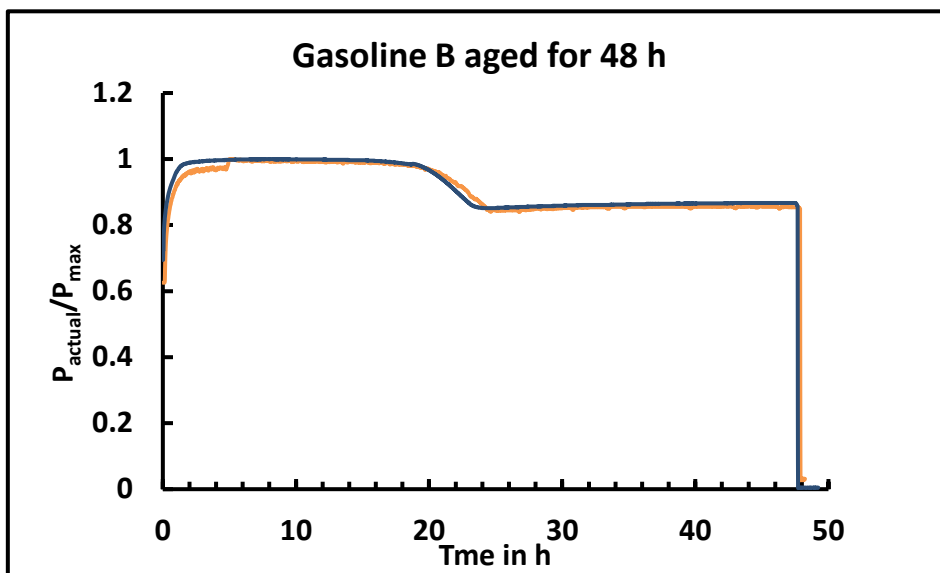


Figure 12 Gasoline B aged for 48 h in BigOxy method

When we compare the 48 h curves of gasoline A and gasoline B, it can be seen that the gasoline A is stable compared to gasoline B. The induction time for gasoline B is 24 h approximately. Whereas the gasoline A requires higher experimental times to exhibit auto-oxidation. The quality of the gasoline also depends on their consistent mixtures which varies for every gasoline. Also, in the oil refinery after the extraction of gasoline, it is added with additives to improve its performance. Therefore, here we can see that the gasoline B's quality is comparatively less than gasoline A in terms of oxidation stability.

### 3.5.3 M100:

From the graph in the Figure 21 of the annexe 1, the M100 sample is behaving similar to the 24 h experiment. The fuel is very stable and there is no pressure drop in the curve. The oxidation stability of M100 is high for 48 h BigOxy experiment. There is no auto-oxidation reaction observed in the liquid phase of the of the fuel. But there will probably

be a reaction in gas phase between gaseous oxygen and methanol vapours. This results in the formation of formaldehyde with water in the gas phase as discussed before.

### 3.5.4 M15 Gasoline A:

From the graph shown in the Figure 13, it can be clearly observed that there is pressure drop after 30 h-32 h approximately. Here the pressure curve started to decrease from 18 h approximately. This means the auto-oxidation has started from 20 h and has ended after 31 h. Therefore, it can be stated that the induction time for M15 Gasoline A is approximately 31 h. It can also be observed that the results are repeatable where the curves are behaving in a similar way. Here the induction time has decreased very significantly after mixing methanol for gasoline A when compared to pure gasoline A (decreased from 63 h to 31 h). This is due to the presence of weak unsaturated bonds in the fuel blend, which is very easy to break and can form alkyl radical very fast. Due to the weak bonding energy, it is very easy for oxygen molecules to diffuse inside the fuels by breaking their bonds and forming alkyl radical. As the availability of alkyl radical is higher, the rate of auto-oxidation reaction is high and therefore the induction time is less. This also depends on the blending properties and chemical bonds in the fuel as well.

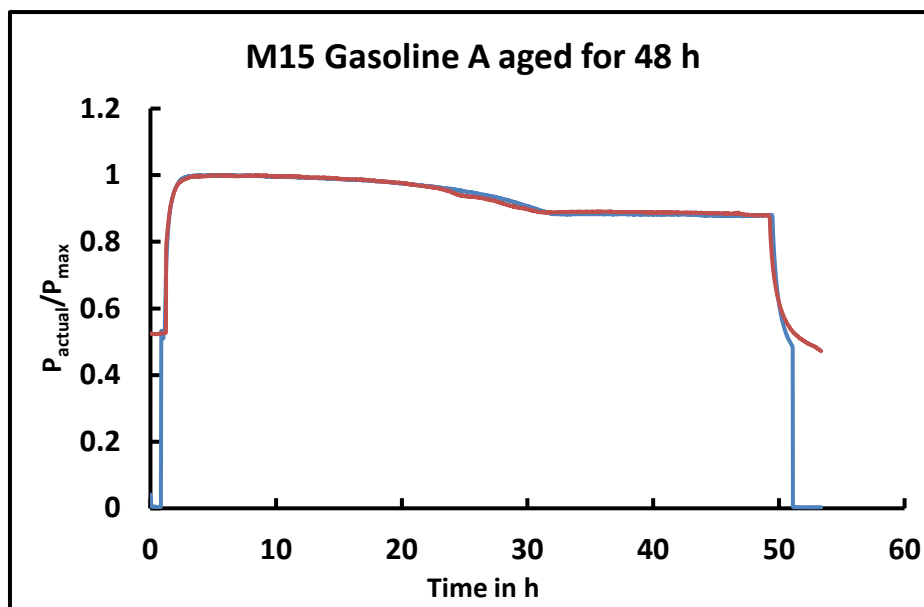


Figure 13 M15 Gasoline A aged for 48 h in BigOxy method

### 3.5.5 M15 Gasoline B:

The graph shown in Figure 14 represents the pressure curves for 48 h experiment for M15 gasoline B blend. Here the auto-oxidation has reached its final stage after the 22 h approximately. Therefore, induction time of BigOxy ageing for M15 gasoline B blend is 22 h approximately. Here the repeatability of the result can also be observed, the induction time for 24 h experiment is almost same for 48 h experiment for M15 Gasoline B (22 h-23 h) which means BigOxy ageing is standardized for M15 Gasoline B.

Here the induction time did not vary very much like it did in M15 gasoline A after mixing methanol. The induction time of M15 gasoline B just decreased by approximately 2 h when we compared to pure gasoline B. Here the weak unsaturated bonds did not increase very much after blending like it did in M15 gasoline A. Therefore, the auto-oxidation rate did not increase very much, where the availability of alkyl radicals did not vary a lot.

When we compare the 48 h results for M15 blends for gasoline A and B, it can be clearly observed that the oxidation stability of the M15 gasoline A is higher than gasoline B. This actually makes sense because, pure gasoline A has higher oxidation stability than pure gasoline B which indicates that the presence of unsaturated bonds is high in gasoline B than in A.

Here the behaviour of both the Gasolines after blending with methanol can be observed. The oxidation stability of gasoline A decreased significantly (decreased by approximately 32 h) compared to pure gasoline A. The oxidation stability of M15 gasoline B decreased slightly compared to pure gasoline B (decreased by approximately 2 h).

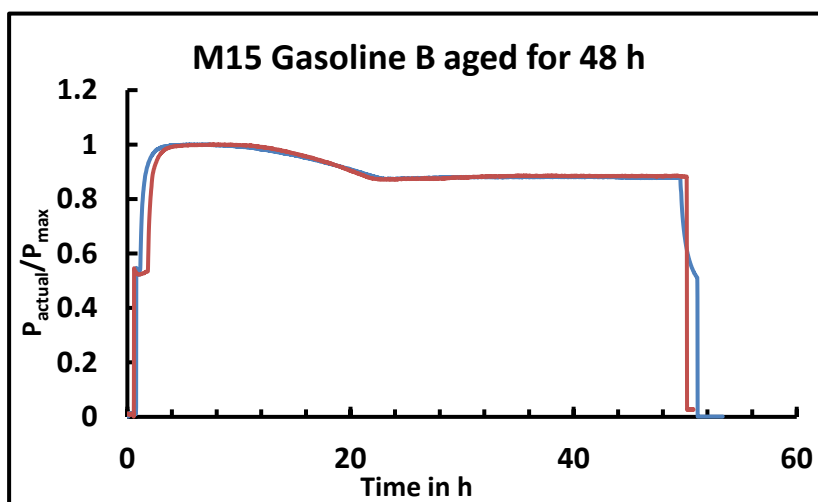


Figure 14 M15 Gasoline B aged for 48 h in BigOxy method

## 3.6 Results for 72 h BigOxy Experiments

### 3.6.1 Gasoline A:

From the graph shown in the Figure 15, gasoline A aged under 5 bar in 95°C for 72 h, it can be observed that here gasoline A exhibited the auto-oxidation reaction with oxygen. The pressure drop is seen after 63 h approximately. Here it can be stated that the induction time required for gasoline A to break the bond (C-H with 413 kJ mol<sup>-1</sup>) and react with gaseous oxygen is approximately 63 h for BigOxy accelerated ageing method. Gasoline A was very stable for both 24 h and 48 h ageing. But it lost its oxidation stability after 63 h in 72 h experiment. It can also be noted that the results are repeatable as two curves are behaving similarly in the Figure 15. Hence, Gasoline A is standardized for BigOxy accelerated ageing method with the induction time of 63 h.

As discussed earlier, gasoline A has higher quality in terms of oxidation stability compared to gasoline B. This means the alkyl radicals are formed faster in gasoline B than in gasoline A. This also indicates that there are more unsaturated weak bonds in gasoline B than in gasoline A.

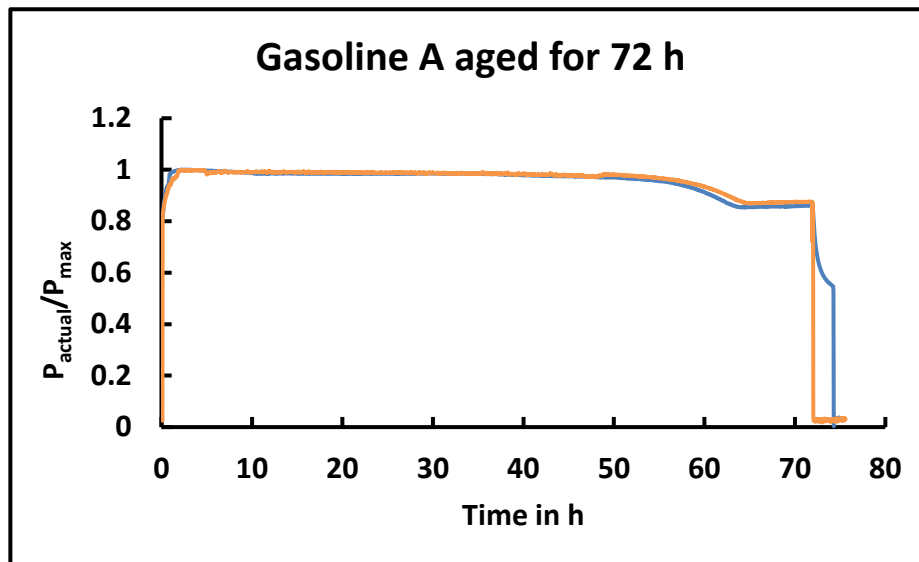


Figure 15 Gasoline A aged for 72 h in BigOxy method

### 3.6.2 Gasoline B:

The graph of Figure 22 from annexe 1, shows pressure curves for gasoline B aged for 72 h under 5 bar at 95°C. As discussed earlier, the standardized induction period for gasoline B for BigOxy ageing is approximately in the range of 24 h-26 h. Likewise, the

curves in the graph of Figure 22 from the annexe 1 shows the same behaviour where the pressure drop was observed at 24 h approximately. This even more validates the repeatability of the results in the BigOxy test bench. Though the induction period is same for 48 h and 72 h gasoline B experiments, there will be a difference in the analytical results (water content and acid value) which is discussed in the further part of this chapter. Because the auto-oxidation duration is higher in 72 h where fuel degradation (auto-oxidation products) will be more than in 24 h and 48 h.

### **3.6.3 M100:**

In the Figure 23 of annexe 1, the graph shown for pure liquid methanol aged for 72 h under 5 bar pressure at 95°C. Methanol exhibits the same behaviour similar to 24 h and 48 h experiments. As explained earlier methanol being most stable molecule [35] with saturated single bond with only two pairs of free electrons makes it stable with bonding energy of 360 kJ/mol [38]. Therefore, the only possible reactions here will be in gas phase between methanol vapours and gaseous oxygen which results in formation of formaldehyde with water vapours. Along with methanol being a stable molecule, the boiling point is pretty low which is 64.7°C [39] and the vapour pressure of the methanol is 0.202 bar [40] at room temperature (30°C). By analysing these properties of methanol, it can be stated that inside the reactor, liquid methanol is not even reaching its boiling point. Though the temperature inside the reactor is 95°C which is greater than methanol's boiling point (64.7°C), but the vapour pressure of methanol is very low (0.202 bar) compared to the 5 bar induced pressure inside the reactor. As the boiling can only happen if the outside pressure is equal or greater to the vapour pressure of the liquid. Therefore, we can conclude that the liquid methanol is having highest oxidation stability in all the 24 h, 48 h and 72 h experiments compared pure Gasolines and M15 Gasoline blends without any pressure drop.

### **3.6.4 M15 Gasoline A:**

From the graph in the Figure 24 of the annexe 1, the pressure curves for M15 gasoline A aged for 72 h under 5 bar at 95°C are shown. The pressure drop is after 28 h-29 h approximately. Here the pressure drop has started nearly after 20 h which is similar in 48 h experiment and the auto-oxidation (initiation and propagation) reactions completed after 28 h-29 h approximately. Therefore, we can say that the results are repeatable for

M15 Gasoline A for BigOxy accelerated ageing with induction period range of 29 h-31 h.

### **3.6.5 M15 Gasoline B:**

As seen in Figure 25 from annexe 1, pressure curves for 72 h experiment for M15 gasoline B under 5 bar at 95°C are shown. The induction period is in the range of 20 h-23 h which is similar to the 24 h and 48 h experiment. Therefore, it can be stated that the results are repeatable when we compare all the three experimental time frames, with the induction period of approximately 23 h for M15 Gasoline B blend for BigOxy accelerated ageing.

As discussed earlier, the behavioural difference in terms of oxidation stability can be seen before and after blending gasoline with methanol. The oxidation stability of gasoline A decreased significantly after adding methanol. This is because the unsaturated weak bonds got increased in the blend after adding methanol, which is the main reason for reduced induction periods. As the bonding energy decreases the stability of the fuel decreases where fuel can readily react with oxygen and undergo auto-oxidation. Here the bonds are broken through the diffusion of gaseous oxygen in the reactor forming alkyl radicals very quickly, resulting in the increased rate of auto-oxidation.

But gasoline B's oxidation stability did not get affected very much after blending. There was a slight decrease in the induction period in the blend. Here the bonding energies did not vary that much leading to formation of unsaturated bonds. Therefore, the auto-oxidation rate did not show any significant increase. Since, the qualities of the gasoline vary, and they are also added with additives in the refinery during extraction to improve their performance. All these factors influence the reaction of gasoline with methanol molecules which affects the blending properties as well. Therefore, here two different oxidation stability behaviours in gasoline A and gasoline B after blending it with methanol can be observed. The oxidation stability got decreased significantly in M15 Gasoline A and did not vary much in M15 Gasoline B.



## 3.7 Oxygen Consumption Calculation

As discussed earlier that there is a reaction of liquid fuel with the gaseous oxygen inside the reactor which is called auto-oxidation. This auto-oxidation is seen the form of pressure drop through pressure curves of the experiments. This indicates the oxygen consumption phase during the auto-oxidation reaction where the liquid fuel consumes oxygen to form auto-oxidation products. It is essential to analyse the amount of oxygen consumed by the liquid fuel with respect to the type of fuel. This gives us a clear understanding on which fuel requires how much oxygen to form auto-oxidation products (absorption capability).

To calculate the amount of oxygen, two assumptions have been done, the first one is assuming that the experiment is conducted in the ideal conditions and the second one is, though there will be oxygen, nitrogen, and other inert gases inside the reactor, it is assumed that only oxygen reacts with fuel and other reactions are neglected. Therefore, only oxygen is consumed by the fuel and amount of the gas reduced in the reactor is equal to amount of oxygen consumed by the fuel. The method of calculation is shown in appendix 2. Since the ideal system is considered, ideal gas equation shown in equation (21) is used.

Using ideal gas equation here:

$$PV = nRT \quad (21)$$

**P** = Pressure (Pa); **V** = Volume (m<sup>3</sup>); **n** = amount of gas (mol)

**R** = Universal gas constant (m<sup>3</sup>.Pa.K<sup>-1</sup>.mol<sup>-1</sup>); **T** = Temperature (K)

The oxygen consumption for each fuel is listed with respect to their experimental durations in the Table 2. All the calculations are done for the same curves (experiments) shown in the BigOxy results of this report which is discussed in the previous part. If carefully observed, the oxygen consumption for each fuel with their experimental times is shown. For gasoline A the oxygen consumption is in the range of 79%-93% (500 mg-560 mg). gasoline B has consumed 96%-97% of oxygen approximately (575 mg-600 mg) in both the experimental time frames (48 h and 72 h) which had pressure drops. M15 gasoline A has consumed 79%-93% of oxygen (500mg-585mg) for both 48 h and 72 h experiments which has pressure drops. M15 gasoline B has consumed 94%-100% of oxygen (560 mg-600 mg) for all the experiments (24 h, 48 h and 72 h) which showed

pressure drops. By analyzing and comparing the oxygen consumption for each fuel, it can be mainly observed that the oxygen consumption of gasoline A and M15 gasoline A is nearly equal which is 79%-93% (500 mg-585 mg). Similarly, the oxygen consumption of gasoline B and M15 gasoline B is nearly equal which is 95%-100% (560 mg-600 mg).

Based on these observations, it can be stated that for the methanol blends of both the gasolines, the methanol has no effect on quantity of oxygen consumption since the oxygen consumptions are same for pure gasoline and their blend with methanol (M15). This indicates that the methanol is stable even inside the gasoline and doesn't react with oxygen in any ways. Methanol has no effect on oxygen consumption in blends, but the oxidation stability of the pure gasolines decreased when methanol was added which means the oxygen consumption (auto-oxidation) was faster in blends than in pure gasolines. One more important observation here is that the experimental durations (24 h, 48 h and 72 h) has no influence on the oxygen consumption of fuels. Since the oxygen consumption is almost equal for each fuel irrespective of their experimental time frames, it can be stated that oxygen consumption is independent of time durations of BigOxy accelerated ageing experiment. Here, the gasoline B and M15 gasoline B has consumed almost complete (100%) oxygen in the reactor compared to gasoline A and its blend. This is in tune with the BigOxy results, where the oxidation stability of gasoline A and M15 gasoline A is higher than gasoline B and M15 gasoline B respectively.

Experimental Duration	Fuel	O <sub>2</sub> consumed (mg)	O <sub>2</sub> consumed (%)	O <sub>2</sub> remaining in the reactor (mg)
24 h	M15 Gasoline B	585.77	100.00%	0
48 h	Gasoline B	599.25	96.01	24.87
	Gasoline B	586.91	97.38	15.77
	M15 Gasoline A	504.35	80.08	119.27
	M15 Gasoline A	532.71	85.69	88.9
	M15 Gasoline B	575.04	94.66	32.39
	M15 Gasoline B	606.37	100	0
72 h	Gasoline A	560	92.8	43.4
	Gasoline A	503.07	79.69	128.13
	Gasoline B	591.54	96.2	23.32
	Gasoline B	575.09	96.78	19.12
	M15 Gasoline A	497.17	79	132.61
	M15 Gasoline A	585.03	93.06	43.58
	M15 Gasoline B	578.81	95.16	29.42
	M15 Gasoline B	564.77	98.15	10.61

Table 2 Oxygen consumption of fuels with respect to their ageing periods

## 3.8 Results for PetroOxy Oxidation Stability

As explained in the chapter 2, petroOxy is one of the approved standard methods to test the oxidation stability of the fuels. It is very important to compare the BigOxy ageing results with PetroOxy to validate our BigOxy ageing method that we have used in this thesis for experiments. This is done to check the quality of the BigOxy aged fuels in terms of their oxidation stability to see the effectiveness of the BigOxy accelerated ageing. The graph in the Figure 16 shows the oxidation stability (min) of the fuel samples for the PetroOxy ageing tests conducted to the BigOxy aged and fresh samples.

Here if the behaviour of Gasoline A is observed, the oxidation stability has decreased with their ageing time. The fresh gasoline A's oxidation stability in the petroOxy is 90.25 min, which has reduced when 24 h, 48 h and 72 h BigOxy aged samples are tested. The main observation is that as the BigOxy ageing period of the fuel increases, their oxidation stability in petroOxy decreases.

For gasoline B, the fresh sample the oxidation stability in petroOxy is 37.53 min. It has decreased for the aged sample, but the oxidation stability is almost same for all the 24 h, 48 h and 72 h aged samples (19 min-24 min). This indicates that the fuel is dead and has no more free radicals to offer for auto-oxidation and has reached its end saturation point. If the fuel has no reaction sites to offer for auto-oxidation reaction, the petroOxy oxidation stability value increases.

Since the pure methanol was stable throughout all ageing experiments that were conducted. The oxidation stability of the 24 h aged methanol sample was 953.65 min (16 h). In PetroOxy for the fuels which has the oxidation stability more than 8 h, it is considered as very stable fuel and considered as >8 h. Therefore, in the Figure 16 it is shown as 480 min (8 h) for all methanol experiments.

It was not possible to determine the oxidation stability for fresh M15 gasoline A. In petroOxy the maximum allowable temperature and pressure test conditions are 140°C and 18 bar respectively. If this limit exceeds while testing, then the apparatus shutdowns automatically. Likewise, for fresh M15 gasoline A, the pressure exceeded 18 bar and the device was automatically switched off. But, as discussed earlier that the M15 gasoline A has the oxidation stability higher than M15 gasoline B. If the oxidation stability

of petroOxy results for BigOxy aged samples are observed, it has reduced with the range of 16min-40min. The oxidation stability (min) has increased in the 72 h aged sample when compared to 24h and 48h samples, this shows that the fuel is completely aged and has no reaction sites (free radicals) to offer for auto-oxidation. Therefore, the oxidation stability value has increased in petroOxy.

If the oxidation stability for M15 gasoline B is observed. The fresh sample has highest oxidation stability compared to aged samples. The petroOxy oxidation stability for aged samples have decreased as the BigOxy ageing duration increased.

From the observation of these results, it can be stated that the fuel degradation increases with respect to their ageing time. This indicates the petroOxy oxidation stability decreases as the BigOxy ageing duration increases when BigOxy aged samples are tested in petroOxy.

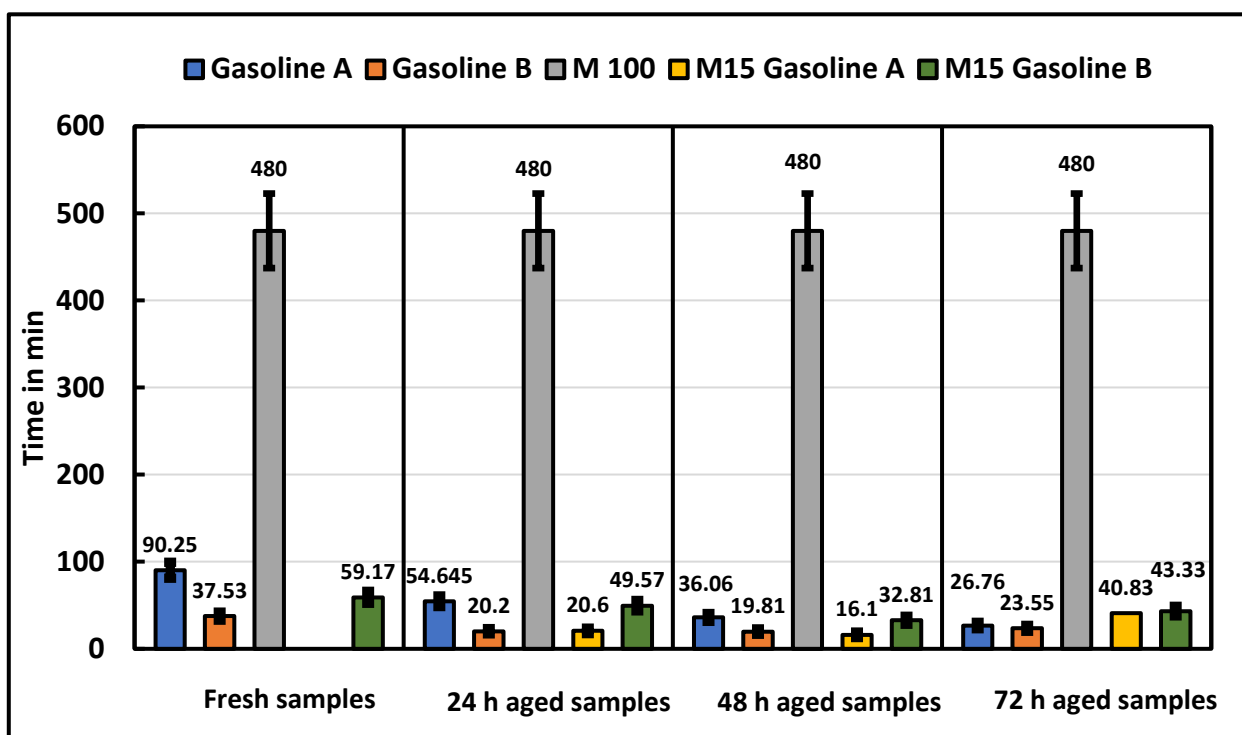


Figure 16 Results of PetroOxy Oxidation Stability

### 3.9 Results for Water Content

As discussed earlier, the phases involved in auto-oxidation reaction mechanism in the chapter 2. If the reactions (22) and (23) mentioned below are observed for the propagation stage reaction mechanism. After the hydroperoxide (ROOH) radical

decomposes, it forms alkoxy (RO•) and hydroxyl radical (OH•) as seen in reaction (22). The hydroxyl radical further reacts with fuel and forms water as seen in reaction (23). Therefore, water is one of the main products obtained in the end of the propagation stage. Therefore, by analysing the water content of aged fuels and fresh fuel samples, the rate of effect of ageing (auto-oxidation) in fuels can be observed.



As seen in the Figure 17, the graph shows the water content (mg/Kg) of the all the fuel samples with respect to their ageing period along with fresh samples. The water content of 24 h aged gasoline A has not changed, it's approximately the same which is in the range of (90mg/Kg-95mg/Kg) for both fresh and 24 h aged sample. Because Gasoline A has the highest induction period (63 h) which means it's water content will not increase significantly until it approaches its induction period (propagation phase). The WC of the 48 h aged Gasoline A is slightly higher than 24 h aged and fresh sample (increased from 95 mg/Kg-104.88 mg/Kg). The WC of the 72-h aged Gasoline A has increased significantly when compared to fresh, 24 h and 48 h samples (increased from 104.88 mg/Kg-323.08 mg/Kg). Here, the maximum increase is seen when the fuel approaches its induction period (63 h). This indicates the propagation reaction happened in 72 h experiment. Gasoline A has the highest induction period out of all fuels we used which showed pressure drop. This is because the water content in fresh gasoline A itself is very low compared to others.

The water content of 24 h aged gasoline B has started to increase slightly when compared to fresh gasoline B (increased to 269.23 mg/Kg from 219 mg/Kg). The WC of 48 h aged gasoline B is significantly higher than the 24 h aged and fresh sample (increased from 269.23 mg/Kg-1019.10 mg/Kg). Since Water content increases due to propagation reaction. Here it can be stated that the fuel has passed its induction time (25 h) and WC content is almost reached its maximum saturation point. Therefore, WC of 72 h aged gasoline B is in the same range of 48 h aged samples (900 mg/Kg-1000 mg/Kg). This indicates that the WC content of gasoline B has increased maximum during 48 h experiment with the induction period of 25 h.

Water content of aged pure methanol has increased to 463.4 mg/Kg compared to fresh

methanol (224.5 mg/Kg). This is due to the hygroscopic property of the methanol to react with water and form mixtures [41]. As discussed earlier that due to formation of formaldehyde and water in the gas phase inside the reactor. After cooling down the water condenses inside which is also one of the reasons for increase in the water content. There are chances that methanol has absorbed some moisture from the atmosphere while transferring the fuel to cannister after the experiment as well. But this does not affect the oxidation stability of the methanol due it's structure as we saw in the BigOxy results. WC of the 48 h aged and 72 h aged M100 is 433 mg/Kg and 497.5 mg/Kg respectively. The WC of M100 is in the range of (400 mg/Kg-500 mg/Kg) for all experiments.

Water content of 24 h, 48 h and 72 h aged M15 gasoline A has increased compared to fresh sample (296.75 mg/Kg). Since its induction period is 31 h, the propagation happens at 48 h experiment. Therefore, if we compare the fresh sample WC and 48 h aged sample WC, there is significant increase (increased from 296.75 mg/Kg- 1268.4 mg/Kg. The WC of the aged M15 Gasoline A is in the range of 1200 mg/Kg-1600 mg/Kg.

The WC of 24 h aged M15 Gasoline B is very high (1487.7 mg/Kg) compared to the fresh sample (89.75 mg/Kg). Since the induction period of the M15 Gasoline B is 23 h, this indicates that the propagation reaction has happened in the 24 h experiment resulting in the maximum WC increase. The WC of the 48 h aged sample and 72 h aged samples are in the range of (1800 mg/Kg- 1900 mg/Kg). Also, M15 Gasoline B has the lowest induction period (23 h) compared to all other fuels used.

By this observation of increasing water content with respect time, it can be stated that the fuel degradation rate also depends on the duration of fuel ageing, where the water content has increased with respect to time. One more important observation is that the water content increase is in tune with the induction period of the fuels. The significant increase (max increase in the WC) is found with respect to the induction periods for all the fuels which had pressure drop.

The main observation here is that the WC in the fuels increases as their ageing duration increases. This indicates that the oxidation stability of the fuels decreases with the increase in WC. But, for methanol the WC remained almost in the same range after ageing (24, 48 and 72 h). This validates the oxidation stability of the methanol as an e-fuel and its compatibility towards long term storage with respect to oxidation stability.

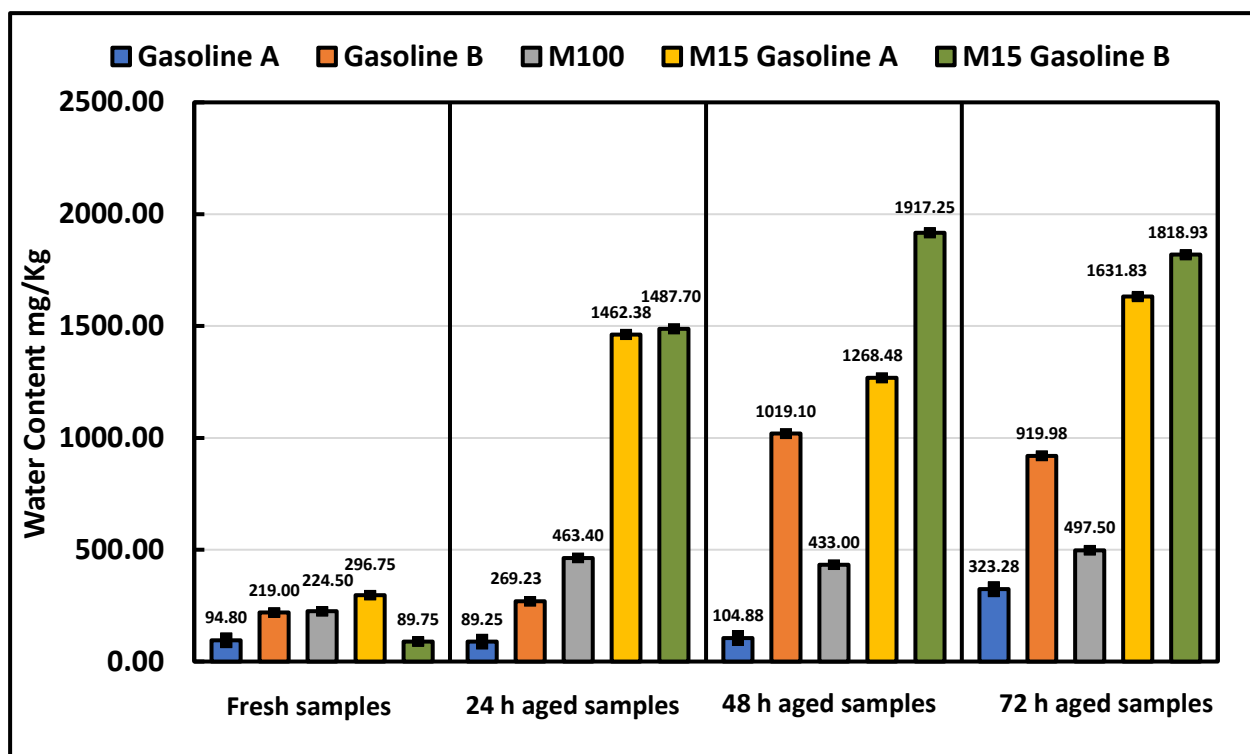


Figure 17 Water Content of the fuels

### 3.10 Results for Acid Content

As discussed in the chapter 2, in propagation reaction, the hydroperoxide radical decomposes to form alkoxy and hydroxyl radicals. Since, hydroxyl radical forms water by reacting with fuel as we know from previous section (Water content). Similarly, the alkoxy radicals form acids, aldehydes and ketones by separation of hydrogen by reacting with fuels as seen in reactions (24) and (25).



Since acid is one of the intermediate products formed in auto-oxidation. In this section the results of acid content analysis are discussed in detail to understand the rate of the effect of auto-oxidation reaction in the fuels. From the graph shown in the Figure 18, the acid content for all the fuels with respect to their ageing period along with the acid content for the fresh fuel samples can be observed.

The acid content (AC) for the gasoline A has increased very significantly in the 65 h experiment compared to fresh sample (from 0.026 mg KOH/gm to 0.301 mg KOH/gm). This indicates that the propagation reaction has occurred in the 72 h experiment which

is in tune with the induction period of Gasoline A (65 h). The AC of 24 h and 48 h aged sample are in the range of (0.07 mg KOH/gm- 0.09 mg KOH/gm) with a slight increase in 48 h from 24 h.

AC of the Gasoline B has increased in 48 h ageing very significantly when compared to the fresh sample (increased from 0.013 mg KOH/gm to 0.672 mg KOH/gm). Since the induction time for Gasoline B is 25 h, the propagation happens in 48 h experiment resulting the maximum increase in the acid content. The AC of the 72 h sample have increased slightly when compared to 48 h (increased from 0.672 mg KOH/gm to 0.928 mg KOH/gm). But the maximum increase is found in 48 h experiment which is in tune with the induction period of Gasoline B (25 h).

The acid content for methanol is in the range of 0.04 mg KOH/gm to 0.5 mg KOH/gm and this does not affect the oxidation stability of the methanol as we know it is a stable molecule. Therefore, acid content has no influence here in accelerated ageing of pure methanol.

The AC of M15 gasoline A has increased significantly in 48 h experiment when compared to fresh sample (increased from 0.068 mg KOH/gm to 0.331 mg KOH/gm). Since the induction time for the M15 Gasoline A is 31 h, the propagation has happened in the 48 h experiment resulting in the maximum increase of AC. The AC of the 72 h experiment is almost in the near range of 48 h aged sample (0.2 mg KOH/gm- 0.3 mg KOH/gm).

The AC of the M15 Gasoline B has a maximum increase in the 24 h experiment when compared to fresh sample (increased from 0.056 mg KOH/gm to 0.624 mg KOH/gm). Since the induction period of the M15 Gasoline B is 23 h, it can be stated that the propagation reaction has happened in the 24 h experiment resulting in the maximum increase of acid content. The AC of 48 h and 72 h experiments are not that different, which is the range of 0.4 mg KOH/gm-0.6 mg KOH/gm.

From these comparisons, it can be concluded by stating that the acid content increases with respect to the ageing time and the maximum increase is found with respect to the induction periods of the BigOxy aged fuels. Therefore, the oxidation stability of the fuel decreases with the increase in AC. But for methanol the AC haven't changed very significantly even after ageing (24, 48 and 72 h). It has maintained the AC in the range of 0.04 mg KOH/gm– 0.5 mg KOH/gm throughout the experiments. This validates the



stable behaviour of methanol towards long term storage with respect to oxidation stability as an e-fuel.

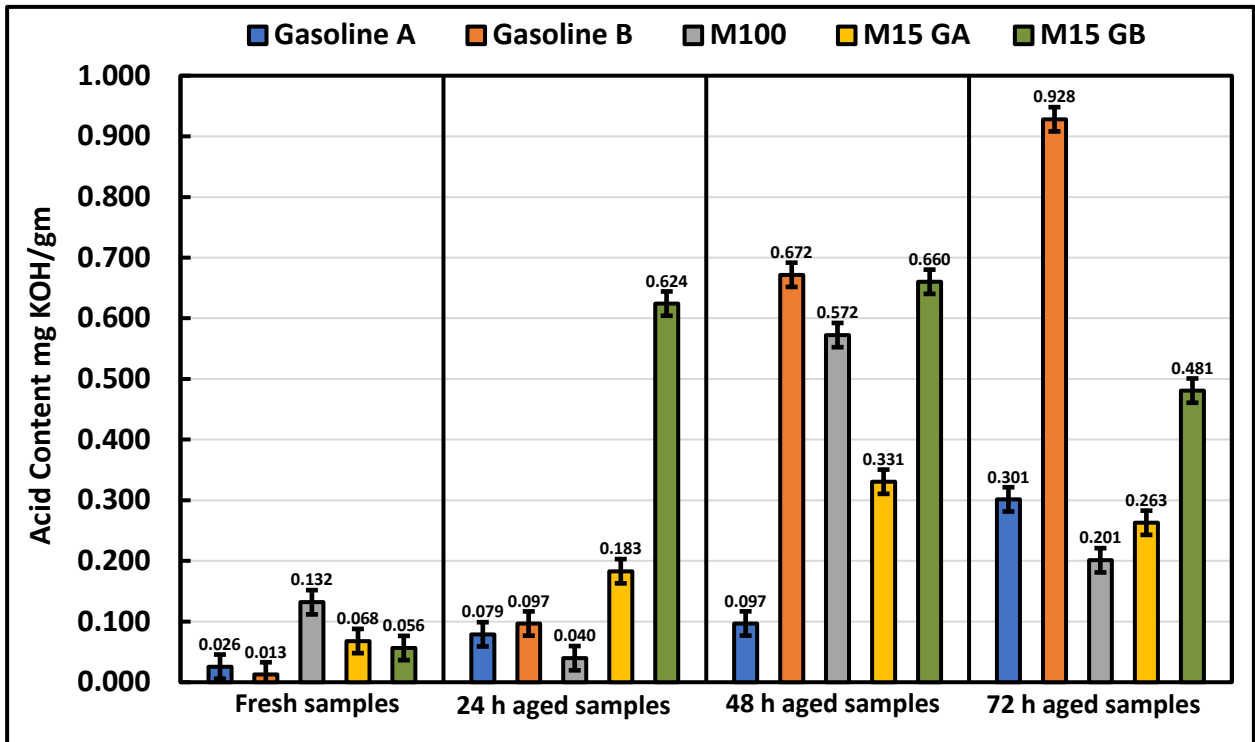


Figure 18 Acid Content of the fuels

# Chapter: 5

## Conclusion and Future works

As discussed in the previous chapter, all the results that were obtained in the experiments that were conducted. In this chapter the main takeaways observed from the results are discussed and concluded. The main aim of this thesis was to study the ageing behaviour of the gasolines (A&B), pure methanol (M100) and their M15 blends with respect to their long-term storage stability/oxidation stability. It involved standardizing the BigOxy accelerated ageing method for methanol, gasoline, and their methanol blends (M15) with respect to their induction period by conducting multiple experiments. It also involved testing the effectiveness of our ageing method and validating it by analyzing the quality of the fuels. It was achieved by conducting analytical tests like acid and water content (products obtained in the auto-oxidation) and PetroOxy oxidation stability test for both aged and fresh samples.

The BigOxy method with 5 bar and 95°C was standardized with respect to the induction periods of the fuels used. The reproducibility of the results in BigOxy method was achieved for 24 h, 48 h and 72 h experimental time frames. Likewise, gasoline A was standardized with the induction period of 63 h-64 h, gasoline B was standardized with the induction period of 24 h-26 h, M15 gasoline A was standardized with the induction period of 29 h-31 h, M15 gasoline B was standardized with the induction period of 21 h-23 h. The oxidation stability of gasoline A was very higher than gasoline B. After mixing pure methanol by 15% vol, the oxidation stability behaviour varied very much in gasoline A resulting in the significant decrease in the induction time of M15 Gasoline A. But the oxidation stability wasn't affected that much in gasoline B after mixing 15% vol methanol, where the induction period was very slightly reduced for M15 gasoline B. As gasolines with two different qualities were used. By observing their results for oxidation stability, it can be concluded that the oxidation stability of the fuel depends on its quality which depends on their properties, where the quality of gasoline A was higher than B in terms of oxidation stability. E-fuel which is Methanol (M100) that we used in the BigOxy

experiment did not show any ageing phenomenon and was stable throughout the 24 h, 48 h and 72 h experiments. There was no pressure drop observed and from this it can be stated that methanol is very stable molecule unlike gasoline. Therefore, the properties of pure methanol make it highly stable fuel in terms of oxidation stability for accelerated ageing methods.

As the fuel consumes the oxygen inside the reactor to form auto-oxidation products, which results in the form of pressure drop in BigOxy method. Therefore, the amount of oxygen consumed by different fuels used were calculated. From the observation of those results, main conclusion is that the amount of oxygen consumed is independent of the ageing duration of fuels. Because oxygen consumption values were same for 24 h, 48 h and 72 h experiments with respect to fuels. The oxygen consumptions also did not vary after blending methanol and gasoline, as it was same for pure and blended gasolines. But in blends the oxygen consumption was faster than in pure gasolines. This is because the oxidation stability decreased after blending methanol. Here it can also be noted that the methanol was stable even in the blends and did not react with oxygen in liquid phase.

After ageing in BigOxy method, the aged samples were tested for their auto-oxidation products (acid and water content) along with their respective fresh samples. From the observation of those results, the conclusion is that the water content and acid content increases as the ageing duration increases. This means the auto-oxidation rate is higher in higher ageing durations, resulting in the increased water and acid content (auto-oxidation products) values. The important take away is that the significant increase in WC and AC was found in the BigOxy induction period of the fuels. The significant increase was in tune with the induction period of all the BigOxy aged fuels. This validates that our BigOxy method is very efficient for the fuels that were used.

The results of petroOxy oxidation stability tests were conducted for fresh samples and BigOxy aged samples. The results showed that the oxidation stability in petroOxy decreases as the fuel degradation in BigOxy increases. This means the auto-oxidation reactions in the BigOxy is very effective resulting in the quality degradation of the fuels.

The main conclusion is that the oxidation stability depends on the quality of the fuel, and it is not possible to blindly predict the oxidation stability of any fuel based on its external factors, appearance etc. It should be tested specifically for the quality in terms of their

oxidation stability. This can only be achieved through conducting specific experiments to study their ageing behaviour and conducting set of analytical tests to understand their quality degradation with respect to their rate of ageing.

Speaking of the analytical tests that were conducted, the quality of oxidation stability is not only the capacity of the fuel to resist the auto-oxidation reaction and form products. It is also the capacity of the fuel to maintain the same amount of water and acid contents (nearly equal to the WC and AC of the fresh sample) even after undergoing ageing or fuel degradation process. This was observed in methanol which was stable in every experiment conducted for ageing and analytics.

Therefore, it can be evidently stated that the BigOxy accelerated ageing method is standardized for methanol, gasoline and their methanol blends. The reproducibility of the results is achieved. The analytical test results for water content and acid content furthermore validates the efficiency of our ageing method. Alongside, the petroOxy oxidation stability results also validate the BigOxy method.

There is a wider scope for accelerated BigOxy ageing method which can be considered for the future research work of this thesis. Since methanol was very stable in all our BigOxy experiments conducted under 5 bar at 95°C. Methanol can be tested with variable pressure conditions (<5 bar) with variable oxygen concentrations inside the reactor. The ageing behaviour of the fuels that were used with variable oxygen concentrations can be analyzed. There is also a scope to study the ageing behaviour of M 85 samples with 85% methanol and 15% gasoline. Since the BigOxy method was standardized with respect to only the induction period of the fuels. This can be further elaborated by studying the ageing behaviour of the fuels by adding the stabilizers like antioxidants and can be standardized the fuels with respect to the antioxidants. BigOxy ageing also allows to test the material compatibility of the fuel. This allows us to study the ageing behaviour of the fuel which is in contact with engine components and the influence of the materials in the components for ageing. A comparative study can also be done by ageing fuel in natural conditions and in BigOxy method. For this the gasoline fuels and some blends of Gasoline with methanol are stored in a regular storage for different time periods. Further the same fresh fuels samples are also tested in the accelerated ageing BigOxy test bench. Thus, comparing the fuels properties between the methods over the course of time, helps in finding a correlation between the accelerated method and the real-life storage of the fuels.

# Bibliography

- [1] L. J. Anthony, Ed., *Information sources in energy technology*. London ; Boston: Butterworths, 1988. ISBN: 978-0-408-03050-2
- [2] M. Owczuk and K. Kołodziejczyk, 'Liquid Fuel Ageing Processes in Long-term Storage Conditions', in *Storage Stability of Fuels*, K. Biernat, Ed. InTech, 2015. doi: 10.5772/59799.
- [3] K. Brendel, S. Eiden, and S. Feldhoff, *Einfluss der Alterung von Mitteldestillaten mit alternativen Komponenten auf die Funktionalität und die Bewertung von Additiven nach No-Harm Kriterien: = Influence of the aging of middle distillates with alternative componants on the functionality and assessment of additives according to No-Harm tests*. Hamburg: DGMK, Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V, 2017.
- [4] Kosuru, Chandra Kanth Mallali, Hichame Ait El and Eiden, Simon, 'Accelerated ageing test bench - BigOxy'. ISBN: 978-3-941721-79-1
- [5] Petrotest Instruments GmbH & Co KG, 'Oxidation-Stability of Diesel & FAME - PetroOXY (automatic)'. [Online]. Available: [https://www.tqsrl.com/wp-content/uploads/petrooxy\\_product\\_13-3000\\_en.pdf](https://www.tqsrl.com/wp-content/uploads/petrooxy_product_13-3000_en.pdf)
- [6] Metrohm, 'Professional Rancimat'. Metrohm. [Online]. Available: [https://www.metrohm.com/en\\_us/products/stability-measurement/Stability-measurement-Rancimat-Thermomat.html](https://www.metrohm.com/en_us/products/stability-measurement/Stability-measurement-Rancimat-Thermomat.html)
- [7] S. Black and J. R. Ferrell, 'Determination of Carbonyl Groups in Pyrolysis Bio-oils Using Potentiometric Titration: Review and Comparison of Methods', *Energy Fuels*, p. acs.energyfuels.5b02511, Jan. 2016, doi: 10.1021/acs.energyfuels.5b02511.
- [8] 'Analytical Methods', in *The Biodiesel Handbook*, Elsevier, 2010, pp. 97–136. doi: 10.1016/B978-1-893997-62-2.50010-3.
- [9] E. Lois, E. L. Keating, and A. K. Gupta, 'Fuels', in *Encyclopedia of Physical Science and Technology*, Elsevier, 2003, pp. 275–314. doi: 10.1016/B0-12-227410-5/00268-4.
- [10] H. Ababneh and B. H. Hameed, 'Electrofuels as emerging new green alternative fuel: A review of recent literature', *Energy Convers. Manag.*, vol. 254, p. 115213, Feb. 2022, doi: 10.1016/j.enconman.2022.115213.
- [11] R. B. Levine, T. Pinnarat, and P. E. Savage, 'Biodiesel Production from Wet Algal Biomass through in Situ Lipid Hydrolysis and Supercritical Transesterification', *Energy Fuels*, vol. 24, no. 9, pp. 5235–5243, Sep. 2010, doi: 10.1021/ef1008314.
- [12] Y. Yun, 'Alcohol Fuels: Current Status and Future Direction', in *Alcohol Fuels - Current*

*Technologies and Future Prospect*, Y. Yun, Ed. IntechOpen, 2020. doi: 10.5772/intechopen.89788.

- [13] S. Aghahosseini Shirazi, B. Abdollahipoor, J. Martinson, B. Windom, T. D. Foust, and K. F. Reardon, 'Effects of dual-alcohol gasoline blends on physiochemical properties and volatility behavior', *Fuel*, vol. 252, pp. 542–552, Sep. 2019, doi: 10.1016/j.fuel.2019.04.105.
- [14] C. Pirola, G. Bozzano, and F. Manenti, 'Fossil or Renewable Sources for Methanol Production?', in *Methanol*, Elsevier, 2018, pp. 53–93. doi: 10.1016/B978-0-444-63903-5.00003-0.
- [15] F. Dalena, A. Senatore, A. Marino, A. Gordano, M. Basile, and A. Basile, 'Methanol Production and Applications: An Overview', in *Methanol*, Elsevier, 2018, pp. 3–28. doi: 10.1016/B978-0-444-63903-5.00001-7.
- [16] J. Czarnocka, A. Matuszewska, and M. Odziemkowska, 'Autoxidation of Fuels During Storage', in *Storage Stability of Fuels*, K. Biernat, Ed. InTech, 2015. doi: 10.5772/59807.
- [17] N. Schubert, Ed., *13th International Colloquium Fuels - Conventional and Future Energy for Automobiles: conference proceedings 2021*. Tübingen: expert, 2021.
- [18] J. Dai and H. Zhang, 'Evidence of undissociated CO<sub>2</sub> involved in the process of C-H bond activation in dry reforming of CH<sub>4</sub>', *J. Catal.*, vol. 410, pp. 266–279, Jun. 2022, doi: 10.1016/j.jcat.2022.04.004.
- [19] G. Naga Venkata Siddartha *et al.*, 'Effect of fuel additives on internal combustion engine performance and emissions', *Mater. Today Proc.*, vol. 63, pp. A9–A14, 2022, doi: 10.1016/j.matpr.2022.06.307.
- [20] A. Sharma and S. Murugan, 'Effect of blending waste tyre derived fuel on oxidation stability of biodiesel and performance and emission studies of a diesel engine', *Appl. Therm. Eng.*, vol. 118, pp. 365–374, May 2017, doi: 10.1016/j.applthermaleng.2017.03.008.
- [21] T. Jia, M. Zhao, L. Pan, C. Deng, J.-J. Zou, and X. Zhang, 'Effect of phenolic antioxidants on the thermal oxidation stability of high-energy-density fuel', *Chem. Eng. Sci.*, vol. 247, p. 117056, Jan. 2022, doi: 10.1016/j.ces.2021.117056.
- [22] H. K. Rashedul, H. H. Masjuki, M. A. Kalam, Y. H. Teoh, H. G. How, and I. M. Rizwanul Fattah, 'Effect of antioxidant on the oxidation stability and combustion-performance-emission characteristics of a diesel engine fueled with diesel-biodiesel blend', *Energy Convers. Manag.*, vol. 106, pp. 849–858, Dec. 2015, doi: 10.1016/j.enconman.2015.10.024.
- [23] S. Ramalingam, S. Rajendran, M. Viswanathan, and V. Duraisamy, 'Effect of antioxidant additives on oxides of nitrogen (NO<sub>x</sub>) emission reduction from annona biodiesel operated diesel engine', in *Advanced Biofuels*, Elsevier, 2019, pp. 247–263. doi: 10.1016/B978-0-08-102791-2.00010-6.
- [24] S. Zabarnick, 'Chemical kinetic modeling of jet fuel autoxidation and antioxidant chemistry', *Ind. Eng. Chem. Res.*, vol. 32, no. 6, pp. 1012–1017, Jun. 1993, doi: 10.1021/ie00018a003.
- [25] 'LOGO! Basic Modules | LOGO! Logic Module | Siemens Global'. <https://new.siemens.com/global/en/products/automation/systems/industrial/plc/logo/logo-basic->

modules.html (accessed Aug. 27, 2022).

[26] 'Grafana: The open observability platform', *Grafana Labs*. <https://grafana.com/> (accessed Aug. 27, 2022).

[27] 'Application PetroOxy: Save on Expensive Antioxidant Additives for Spark-Ignition Fuels :: Anton-Paar.com'. <https://www.anton-paar.com/corp-en/products/applications/application-petrooxy-save-on-expensive-antioxidant-additives-for-spark-ignition-fuels/> (accessed Jul. 11, 2022).

[28] Metrohm, '893 Professional Biodiesel Rancimat'. Metrohm. [Online]. Available: [https://www.metrohm.com/en\\_us/products/stability-measurement/Stability-measurement-Rancimat-Thermomat.html](https://www.metrohm.com/en_us/products/stability-measurement/Stability-measurement-Rancimat-Thermomat.html)

[29] 'OELCHECK: oxidation stability fuel'. <https://en.oelcheck.com/analyses/test-methods/oxidation-stability-fuel/> (accessed Aug. 10, 2022).

[30] L. Botella, F. Bimbela, L. Martín, J. Arauzo, and J. L. Sánchez, 'Oxidation stability of biodiesel fuels and blends using the Rancimat and PetroOXY methods. Effect of 4-allyl-2,6-dimethoxyphenol and catechol as biodiesel additives on oxidation stability', *Front. Chem.*, vol. 2, 2014, Accessed: Aug. 10, 2022. [Online]. Available: <https://www.frontiersin.org/articles/10.3389/fchem.2014.00043>

[31] 'Kinematic viscometer: SVM :: Anton-Paar.com'. <https://www.anton-paar.com/corp-en/products/details/svm-series/> (accessed Sep. 02, 2022).

[32] E. R. Streva, V. M. D. Pasa, and J. R. Sodr , 'Aging effects on gasoline–ethanol blend properties and composition', *Fuel*, vol. 90, no. 1, pp. 215–219, Jan. 2011, doi: 10.1016/j.fuel.2010.07.056.

[33] T. Kaltschmitt and O. Deutschmann, 'Fuel Processing for Fuel Cells', in *Advances in Chemical Engineering*, vol. 41, Elsevier, 2012, pp. 1–64. doi: 10.1016/B978-0-12-386874-9.00001-4.

[34] K. Wang, B. Yuan, G. Ji, and X. Wu, 'A comprehensive review of geothermal energy extraction and utilization in oilfields', *J. Pet. Sci. Eng.*, vol. 168, pp. 465–477, Sep. 2018, doi: 10.1016/j.petrol.2018.05.012.

[35] M. De Falco and M. Capocelli, 'Direct Synthesis of Methanol and Dimethyl Ether From a CO<sub>2</sub>-Rich Feedstock: Thermodynamic Analysis and Selective Membrane Application', in *Methanol*, Elsevier, 2018, pp. 113–128. doi: 10.1016/B978-0-444-63903-5.00005-4.

[36] S. Lervold, R. L deng, J. Yang, J. Skjelstad, K. Bingen, and H. J. Venvik, 'Partial oxidation of methanol to formaldehyde in an annular reactor', *Chem. Eng. J.*, vol. 423, p. 130141, Nov. 2021, doi: 10.1016/j.cej.2021.130141.

[37] B. Waluyo, M. Setiyo, Saifudin, and I. N. G. Wardana, 'Fuel performance for stable homogeneous gasoline-methanol-ethanol blends', *Fuel*, vol. 294, p. 120565, Jun. 2021, doi: 10.1016/j.fuel.2021.120565.

[38] P. Margaretha, 'Chemie der Kohlenstoffverbindungen', in *Chemie f r Mediziner*, Berlin, Heidelberg: Springer Berlin Heidelberg, 2002, pp. 77–172. doi: 10.1007/978-3-642-55960-0\_2.

[39] N. A. Ghyadh, S. H. Hammadi, and H. A. K. Shahad, 'Using solar collector unit in a methanol-

water vapor absorption cooling system under iraqi environmental conditions', *Case Stud. Therm. Eng.*, vol. 22, p. 100749, Dec. 2020, doi: 10.1016/j.csite.2020.100749.

[40] T. Log and A. Moi, 'Ethanol and Methanol Burn Risks in the Home Environment', *Int. J. Environ. Res. Public Health*, vol. 15, no. 11, p. 2379, Oct. 2018, doi: 10.3390/ijerph15112379.

[41] S. Verhelst, J. W. Turner, L. Sileghem, and J. Vancoillie, 'Methanol as a fuel for internal combustion engines', *Prog. Energy Combust. Sci.*, vol. 70, pp. 43–88, Jan. 2019, doi: 10.1016/j.pecs.2018.10.001.



# Annexe 1

## Graphs for BigOxy aged samples

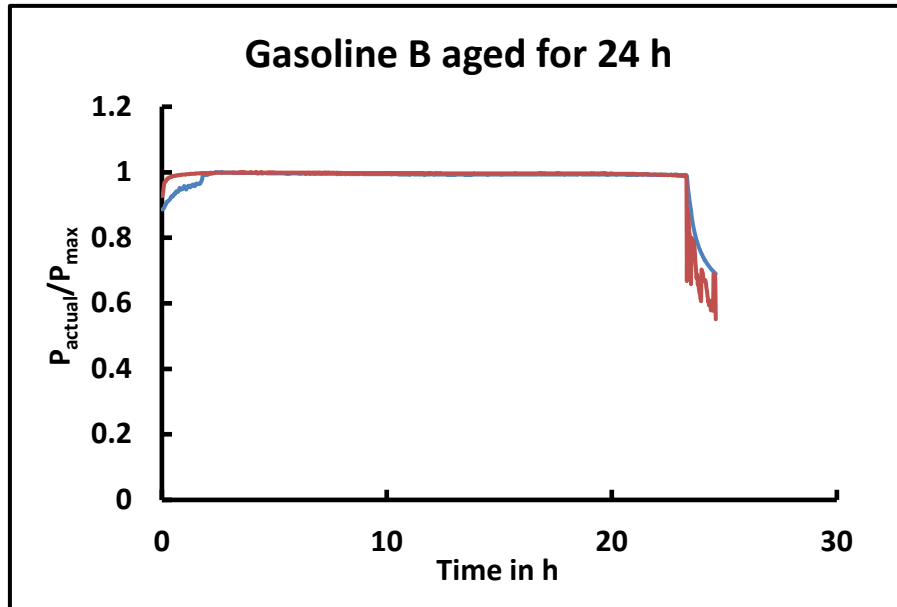


Figure 19 Gasoline B aged for 24 h in BigOxy method

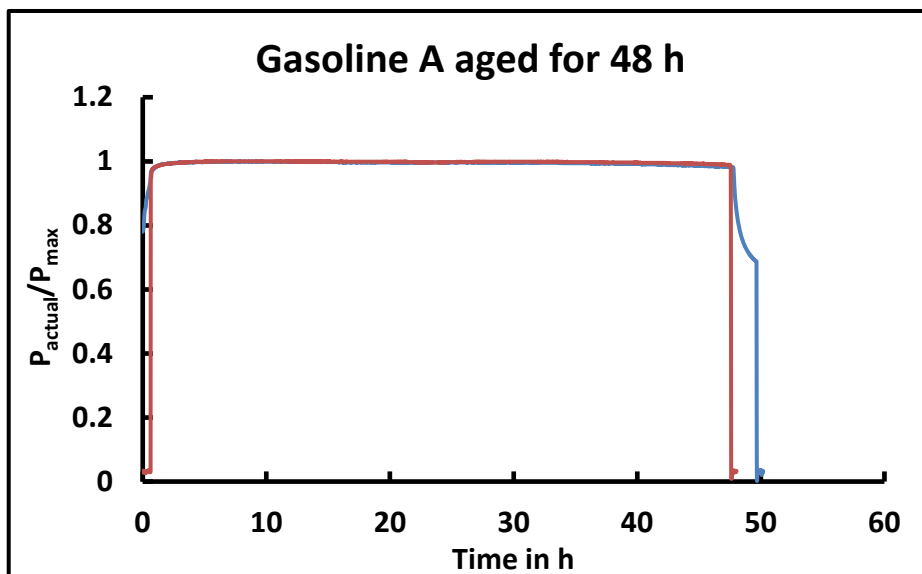


Figure 20 Gasoline A aged for 48 h in BigOxy method

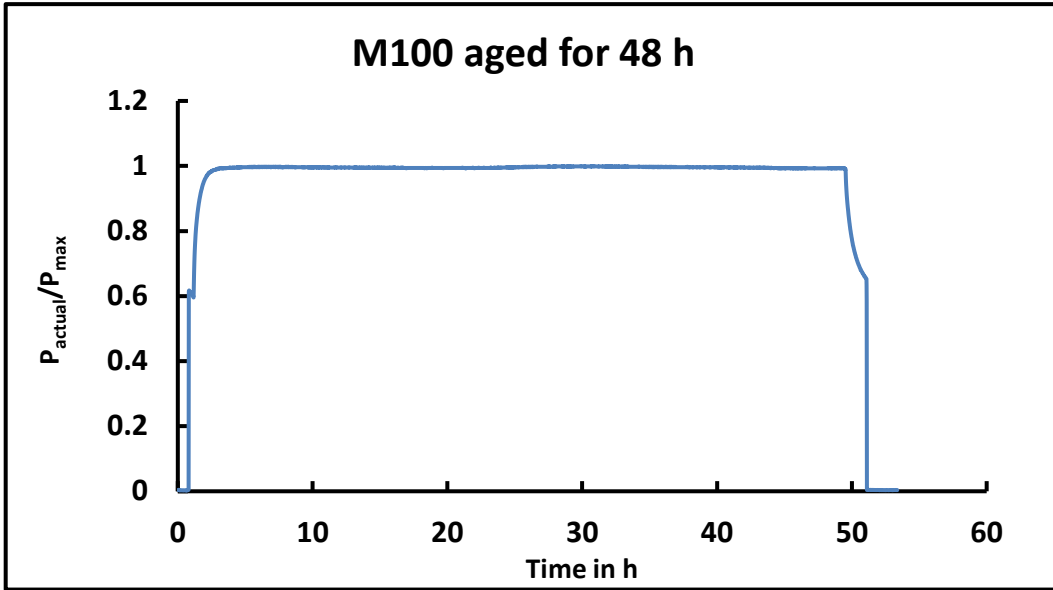


Figure 21 M100 aged for 48 h in BigOxy method

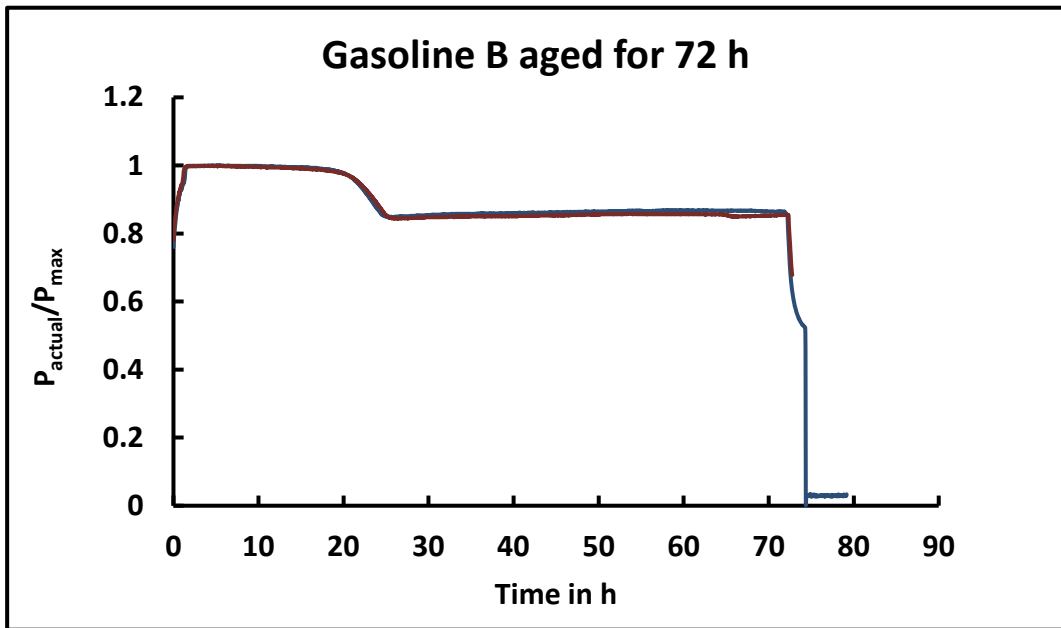


Figure 22 Gasoline B aged for 72 h in BigOxy method

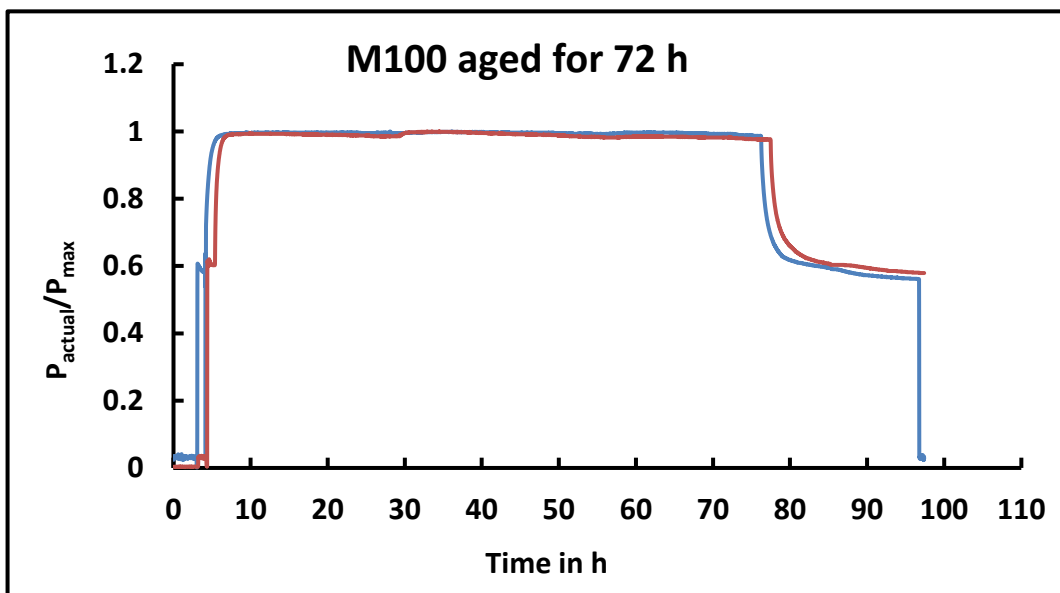


Figure 23 M100 aged for 72 h in BigOxy method

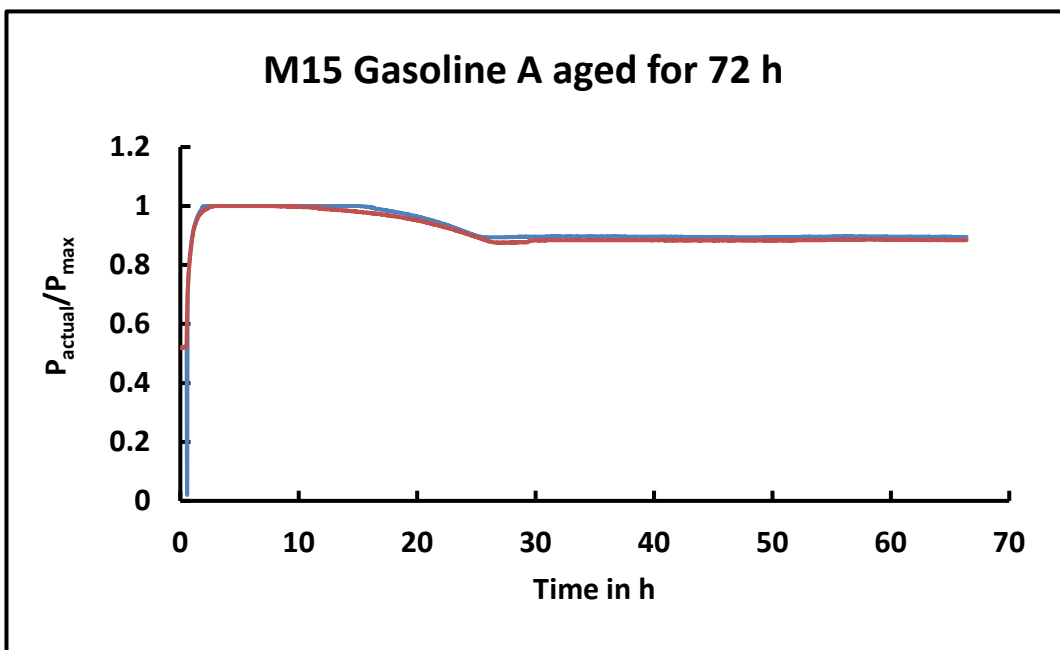


Figure 24 M15 Gasoline A aged for 72 h in BigOxy method

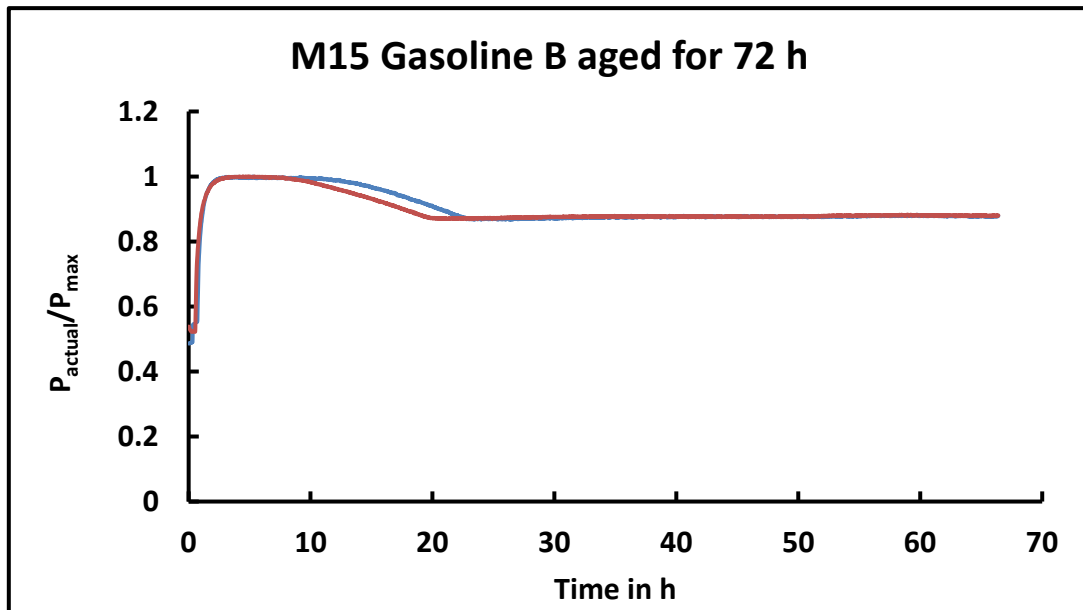


Figure 25 M15 Gasoline B aged for 72 h in BigOxy method

# Annexe 2

## Oxygen Consumption Calculations

**Phase 1 (initial):** This is the very initial phase where the BigOxy reactors are filled 500ml of fuel and not yet kept inside the heating oil bath. They are filled with 5 bar pressure before keeping it inside the heated oil bath. By applying ideal gas equation here:

$$P_{initial} = 5.1 \text{ bar} = 5.1 \times 10^5 \text{ Pa}$$

$V = 500 \text{ ml} = 5 \times 10^{-4} \text{ m}^3$ , this is constant throughout the calculation.

$R = 8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  (Universal gas constant)

$$T_{initial} = 30.5^\circ\text{C} = 303.65 \text{ K}$$

$n_{O_2_{initial}}$  = amount of oxygen in the reactor (to find)

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n_{dry \text{ air}} = \frac{5.1 \times 10^5 \text{ Pa} \times 5 \times 10^{-4} \text{ m}^3}{8.314472 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 303.65 \text{ K}} = 0.101 \text{ mol}$$

$$m_{dry \text{ air}_{initial}} = 28.96 \text{ g} \cdot \text{mol}^{-1} (\text{molar mass of dry air}) \times 0.101 \text{ mol} = 2.925 \text{ g}$$

$$n_{O_2_{initial}} = 0.21 (\% \text{ of } O_2 \text{ in dry air}) \times 2.925 = 0.6142 \text{ g} = 614.2 \text{ mg}$$

**Phase 2 (maximum):** This is the phase where the pressure and temperature become maximum after the reactor is kept inside the heating oil bath.

$$P_{max} = 8.25 \text{ bar} = 8.25 \times 10^5 \text{ Pa}$$

$$T_{max} = 98.1^\circ\text{C} = 371.25 \text{ K}$$

Applying the ideal gas equation as shown before and find  $n_{O_2_{max}}$ :

$$m_{dry\ air_{max}} = 28.96\ g.m^{-1}(\text{molar mass of dry air}) \times 0.133\text{mol} = 3.870\ g$$

$$n_{O_2_{max}} = 0.8127\ g = 812.7\ mg$$

**Phase 3 (final):** This is the phase after the pressure drop is observed which means after auto-oxidation reaction has occurred inside the reactor. In this phase the pressure decreases and becomes stable (after the sufficient amount of oxygen is consumed by the fuel).

$$P_{final} = 7.06\ bar = 7.06 \times 10^5\ Pa$$

$$T_{final} = 98.3^\circ C = 371.45\ K$$

Applying the ideal gas equation as shown before and find  $n_{O_2_{final}}$ :

$$m_{dry\ air_{final}} = 28.96\ g.m^{-1}(\text{molar mass of dry air}) \times 0.114\text{mol} = 3.310\ g$$

$$n_{O_2_{final}} = 0.6951\ g = 695.1\ mg$$

Amount of oxygen consumed,

$$n_{O_2_{consumed}} = m_{dry\ air_{max}} - m_{dry\ air_{final}} = 0.5600\ g = 560.014\ mg$$

Amount of  $O_2$  remaining,  $n_{O_2_{remaining}} = n_{O_2_{initial}} - n_{O_2_{consumed}} = 0.0542\ g = 54.24\ mg$

$$\% \text{ of } O_{2_{consumed}} = 1 - \frac{n_{O_2_{remaining}}}{n_{O_2_{initial}}} = 91.1\%$$

