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

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October 2022

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 blends (M15). 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 and Induction Period

1. Introduction

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]. 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 fuels [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]. In this report, the methods used to study the ageing phenomenon, and factors responsible for the ageing of gasoline, e-fuels, and their blends are discussed.

1.1 Methanol as an e-fuel

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 or electrofuels are considered as potential future fuels capable of replacing fossil fuels and can influence pollution reduction for wellness of our posterity. Fuels like bioethanol, methanol and butanol gained its importance even during 1970's oil crisis [4].

Alcohols are considered as the best alternative for petroleum fuels for transportation sector. Methanol (CH_3OH) or Methyl alcohol (MeOH) is one of the simplest of alcohols and is a colorless liquid having a bit pungent odor. Methanol is considered as one of the very important platforms for chemicals where we can derive several fuels and additives by further chemical processing. In recent days, Methanol is considered as one of the future transportation fuel [5] which can be used alone or mixed with gasoline. When mixed methanol, 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, NOx, SOx and other particulate matters [5]. Since methanol is a hydrogen carrier, it can also be used in automotive field for the fuel cell vehicle (FCV) development [5]. Liquid methanol is becoming very popular in the energy storage field and has also become an alternative for hydrogen [6]. Methanol is also a starting product for many e-fuels.

2. 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". 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 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. 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 [7]. The radical mechanisms involve 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 [7], [8].

2.1 Initiation Reaction

$$\text{R-H} + \text{Initiator (light, temperature or catalyst)} \rightarrow \text{R}\bullet + (\text{H}\bullet)\ [7]$$

$$RH + O_2 \rightarrow HOO\bullet + R\bullet$$

The first stage in exothermic auto-oxidation reaction mechanism is called initiation reaction and it is the slowest reaction that forms R •, which is the hydrocarbon alkyl radical. 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.

2.2 Propagation Reaction

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet$$

$$ROOH \rightarrow RO\bullet + \bullet OH$$

$$RO\bullet + RH \rightarrow ROH + R\bullet$$

$$\bullet OH + RH \rightarrow H_2O + R\bullet$$

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. Then the peroxide radical reacts with fuel (RH) to form the hydroperoxide radical (ROOH). The hydroperoxide radical decomposes leading to the formation of alkoxy (RO•) and hydroxyl (•OH) active radicals. Further the hydroxyl radicals react with fuel (R-H) to form water and alkoxy radicals react with fuel to form acid, aldehydes, ketones and alcohols, which affects performance of the fuels in a negative way. The propagation reaction is fast and self-propagated compared to initiation.

2.3 Termination Reaction

$$R\bullet + R\bullet \rightarrow R\text{-}R$$

$$RO_2\bullet + RO_2\bullet \rightarrow ROOR + O_2, \text{ (inactive products) [7]}$$

$$R\bullet + R\text{-}O\text{-}O\bullet \rightarrow ROOR$$

$$RO\bullet\ (\text{or } ROO\bullet) + ROOH \rightarrow \text{different products}$$

ROOH → Non radical products

The last stage reaction in the auto-oxidation mechanism is termination reaction. Here the two free radicals (R •) and (RO_2•) 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 temperature range for the auto-oxidation to occur is around 30°C-120°C [7]. As the initial auto-oxidation rate is slow, because the availability of the free radicals is low and as a result the changes occur slowly [2], [9], [10]. 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 [7].

3. Additives and Stabilizers

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 [11]. 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 is used 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 NOx emissions when it is added with biodiesel, nano additives like Al_2O3 and TiO_3 is used to improve the thermal efficiency of the brake and to reduce CO emissions [11].

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 [12]. 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.

4. Accelerated Ageing

Accelerated ageing methods are used to forecast the behavior of the liquid fuels in shorter time period. The primary purpose of any fuel is to store the energy and use it when necessary. The fuel should be stable and feasible for the storage and transportation. As

the current focus is on alternative fuels to control and reduce air pollution. Likewise, there are lot of research going on in the development of alternative fuels like oxy methylene ether (OME), methanol to gasoline (MTG) and several other alcohol blends with diesel etc.

Therefore, it is very necessary to also know the behavior of these alternative fuels during its long-term storage [10] 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, BigOxy can be used to test the quality of fuels. PetroOxy and Rancimat are analytical methods and BigOxy is an accelerated ageing method. But all these methods are used to determine the oxidation stability of the fuel and study their ageing behaviors.

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 Oxy-methylene ether (OME), alcohol blends etc., [3].

4.1 The BigOxy Test Bench

Figure 1: The BigOxy test bench setup

This is a modern accelerated ageing method developed by Tec4Fuels. Figure 1 shows the BigOxy test bench setup. This method enables us to test the long-term storage oxidation stability behavior of the fuels like diesel, biodiesels (Fatty acid methyl ester-FAME), gasoline fuels, cooling fluids and lubricants. This method was used to perform all the ageing experiments as a part of this thesis.

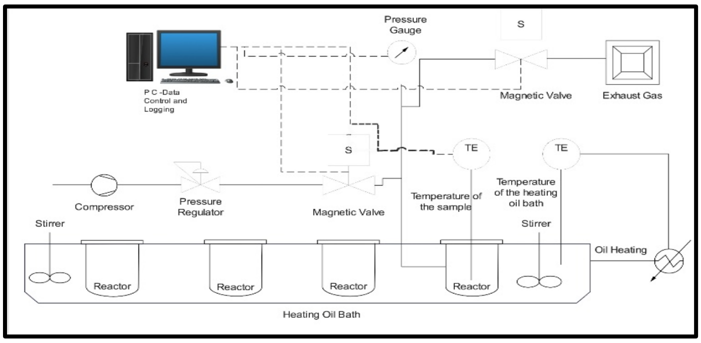

Figure 2: Piping and instrumentation diagram of the BigOxy test bench

In the Figure 2, 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.

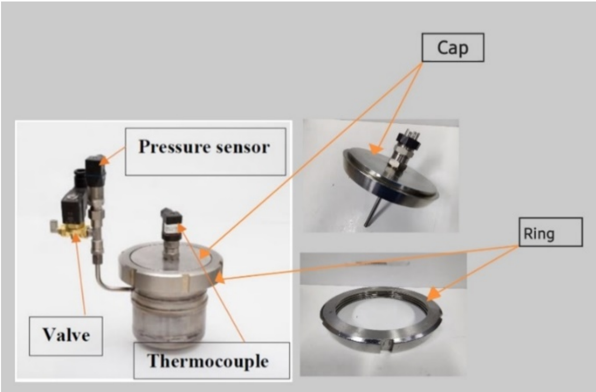

Figure 3: Components of BigOxy reactor

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.

The Figure 3 shows the BigOxy stainless-steel reactor has the maximum volume of up to 1.5 liter 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 autooxidation) 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 max of 180°C. In all the experiments conducted for this thesis, the temperature of the fluid inside the reactor was 95°C with 5 bar induced pressure.

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 reactors are closed tightly after filling them with new fuel samples 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 plots data with respect to the time is examined and the aged fuel sample is used for the further chemical laboratory analysis.

4.1.1 Data Analysis in BigOxy Experiment

The monitoring of the real time temperature and pressure occurs throughout the experimental period. In the Figure 4 and Figure 5 are shown the pressure and temperature curves obtained respectively from the BigOxy experiment which is plotted as the function of time.

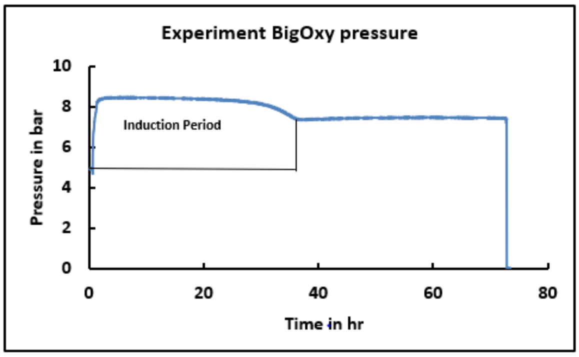

Figure 4: Pressure curve of the BigOxy experiment

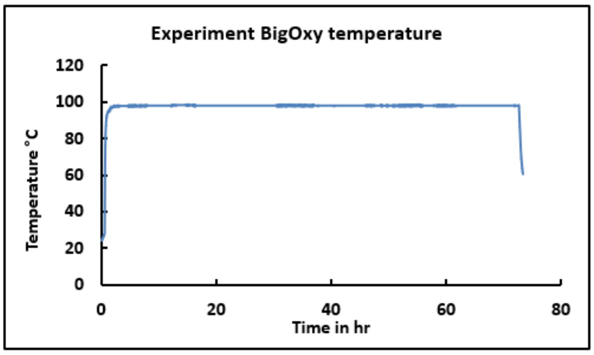

Figure 5: Temperature curve of the BigOxy experiment

Figure 4 represents the gas phase pressure plot profile during 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 kept inside hot oil bath) until the end of pressure drop is observed inside the reactor is referred to as the induction period [10].

4.1.2 Fluid Analysis

After the samples are aged through BigOxy method, they should be tested in the chemical laboratory to identify the quality changes of the fuel after ageing. This is to study the changes in physio chemical properties due to the ageing. 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 [10]. There are some analytical tests like Acid content (AC) (DIN EN 141 04), Water content (WC) (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 provides a scope to check the efficiency of the stabilizers, property improvers which are additives.

4.1.3 Reproducibility

It is very crucial to check the precision of the results that is obtain in the BigOxy test bench. 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 ±1°C. Further, the same sample is tested multiple times to compare the reproducibility of the result.

4.1.4 Applications of BigOxy

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

5. Aim and Research Methodology

The main aim of this thesis is to study the ageing behavior of the liquid fuels like gasoline, methanol, and their blends. This is achieved by conducting the accelerated ageing experiments for the fuels and determining their induction period for each fuel. Since BigOxy is a new method, it is very essential to establish the standards for the test results (induction periods) that are obtained for the fuels.

After this, the BigOxy method is validated by conducting laboratory analytics (PetroOxy, water and acid contents). The fuels are tested for their oxidation stability, they are also tested for their change in water and acid contents.

All the analytical tests are conducted for both BigOxy aged samples and fresh samples to clearly study and understand the quality changes in the fuel after ageing by comparing results of fresh fuel samples. This comparison also gives an idea of how effective the BigOxy method is.

The fuels are tested in BigOxy with respect to three time frames of experimental durations which are 24 h, 48 h and 72 h. Multiple experiments of 24 h, 48 h and 72 h experiments have been conducted for all the fuels used to check how repeatable the results are, the repeatability was checked with respect to the pressure drop durations (Induction periods).

5.1 Fuels used for the experiments

5.1.1 Gasoline

In this thesis, two types of gasolines with different qualities namely Gasoline A and Gasoline B are used to study their ageing behaviors.

5.1.2 Pure Liquid Methanol (M 100)

In the current topic, focus is on the implementation of e-fuels in the BigOxy ageing. It is very essential to study their long-term storage and ageing behavior. Therefore, the methanol (e-fuel) is used in all the experiments of this thesis. Likewise, 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 [6]. Therefore, the methanol quality remains almost same, and the effects are negligible.

5.1.3 M15 Blends for Gasoline and Methanol

The third type of fuel that is used is a blend of Gasoline+Methanol. Since 500 ml 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 being used, blends of both M15 gasoline A and M15 gasoline B are used to test in the BigOxy experiments.

6. Results and Discussions

6.1 BigOxy results for Gasoline A

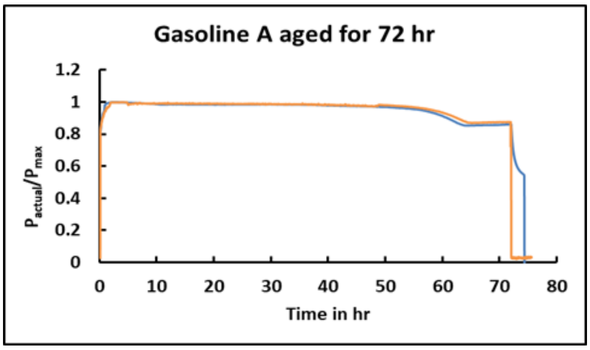

Figure 6: Gasoline A aged for 72 h in BigOxy method

Figure 6 shows the pressure curves for gasoline A aged in BigOxy method. Each curve in the graph represents the individual reactor used for the specific experiment. The x-axis represents time (h) and y-axis represents the normalized pressure values (P_{actual}/P_{max}) in bar. Since many reactors are 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_{actual}) with max pressure value (P_{max}) obtained for each reactor during a specific experiment. For the 24 h and 48 h experiment conducted for gasoline A with 5 bar pressure and 95 °C, it was observed that the pressure was stable throughout the experiment durations (24h and 48h). The absence of pressure drop indicates that the auto-oxidation reaction is absent due to the unavailability of alkyl radical. Therefore, the oxidation stability of Gasoline A is high for both 24 h and 48 h experiments.

From the graph shown in the Figure 6, represents gasoline A aged under 5 bar in 95 °C for 72 h, gasoline A has exhibited the auto-oxidation reaction with oxygen. The pressure drop is seen after 62 h approximately. The induction time required for gasoline A to break the bond (C-H with 413 kJ mol^{-1}) and react with gaseous oxygen is approximately 63 h for BigOxy accelerated ageing method. The results are also repeatable as the two curves are behaving similarly in the Figure 6. Therefore, gasoline A is standardized for BigOxy accelerated ageing method with the induction time of 63 h.

6.2 BigOxy results for Gasoline B

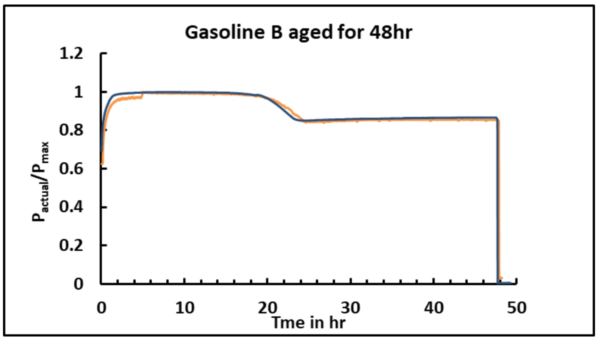

Figure 7: Gasoline B aged for 48 h in BigOxy method

Gasoline B was stable in 24 h BigOxy ageing experiment. No pressure drop was observed for 24 h experiment. This means that the gasoline B needs more energy and induction time (>24 h) to break their bonds and react with oxygen inside the reactor by forming alkyl radical.

Figure 7 shows the graph for the 48 h BigOxy aged experiment of gasoline B. There is pressure drop after 24 h-26 h approximately. Gasoline B also showed the similar behavior in 72 h experiment with the pressure drop after 24 h-26 h.

By comparing the results of gasoline A and B, gasoline A has better quality in terms of oxidation stability than gasoline B. The induction period of gasoline A is 63 h and gasoline B's induction period is 25 h approximately. Probably there are more unsaturated weak bonds in gasoline B than in gasoline A, where the alkyl radical is formed very quickly in gasoline B than in A.

6.3 BigOxy results for Methanol (M100)

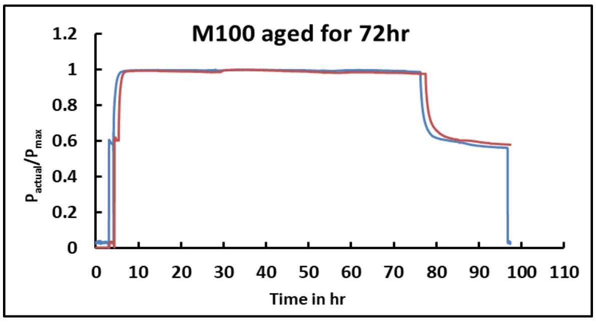

Figure 8: M100 aged for 72 h in BigOxy method

Figure 8 shows the pressure curves for the 72 h BigOxy experiment for liquid methanol. Methanol was stable in all the experiments conducted (24 h, 48 h and 72 h). There was no pressure drop observed in any experiment of methanol. It really makes sense for the absence of pressure drop; as methanol being a pure molecule with saturated single bonds having only one methyl group linked to hydroxyl group [15], definitely should make it more stable than gasoline in BigOxy experiment. In terms of auto-oxidation, methanol did not react with oxygen inside the reactor, and there was no alkyl radical formation to form auto-oxidation products by consuming oxygen.

From BigOxy, though there is no auto-oxidation reaction in the liquid phase, but there could be reaction of methanol with oxygen in the gas phase. Methanol vapors reacts with gaseous oxygen and can form formaldehyde (CH_2O) and water [16] as shown in below chemical reaction (1).

$$CH_3OH + \frac{1}{2} O2 \rightarrow CH_2O + H_2O \qquad (1)$$

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. Although the vapor pressure of methanol at 5 bar is less.

6.4 BigOxy results for M15 Gasoline A

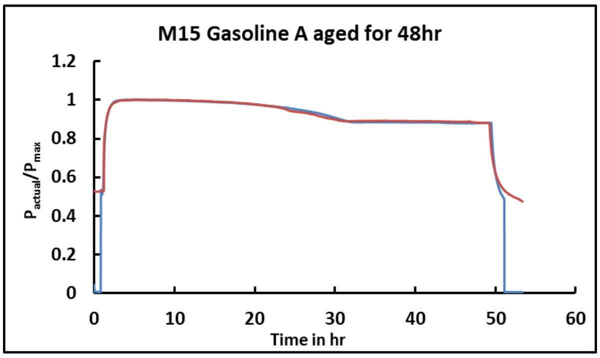

Figure 9: M15 Gasoline A aged for 48 h in BigOxy method

M15 Gasoline A was stable in 24 h experiment and did not show any pressure drop. But, in 48 h and 72 h experiments, there was pressure drop seen after 30 h-32 h and 28 h-29 h respectively. This indicates that there was auto-oxidation reaction in M15 Gasoline A after 29 h-31 h approximately. The alkyl radicals were formed and the oxygen inside the reactor was consumed by the fuel with the induction period of 29 h-31 h approximately. M15 gasoline A behaved almost in a similar way in both 48 h and 72 h experiments and from the Figure 9 the curves are almost coinciding with each other. M15 Gasoline A is standardized in BigOxy ageing with the induction period of 29 h-31 h.

6.5 BigOxy results for M15 Gasoline B

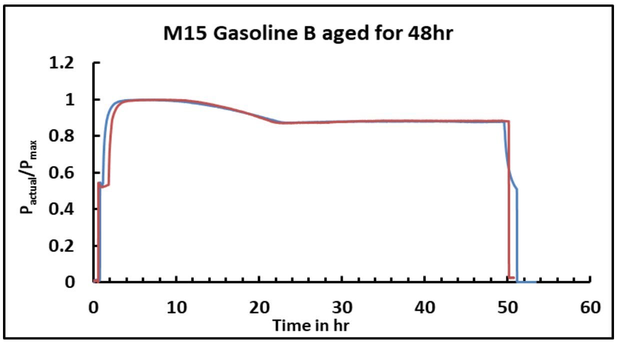

Figure 10: Gasoline B aged for 48 h in BigOxy method

Figure 10 shows the pressure curves for M15 gasoline B aged for 48 h in BigOxy method. M15 gasoline B exhibited pressure drop in all the experiments and the pressure curves behaved almost in a similar way. The induction time of M15 gasoline B in 24 h experiment was nearly 23 h, 22 h for 48 h experiment and 20 h-23 h in 72 h experiment. From these observations, there was auto-oxidation with M15 Gasoline B, in all the experiments by consuming oxygen inside the reactor and forming alkyl radical. Therefore, the results are repeatable, and M15 gasoline B can be standardized with the induction period of 22 h-23 h in BigOxy ageing.

By comparing the results of M15 gasoline A and M15 gasoline B, M15 gasoline A has higher oxidation stability than M15 gasoline B. Because the induction period of M15 gasoline A was nearly 29 h-31 h and M15 gasoline B was 22 h-23 h. This indicates the alkyl radicals are formed faster in M15 gasoline B than in M15 gasoline A. 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.

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. The bonding energies did not vary leading to formation of unsaturated bonds. Therefore, the auto-oxidation rate did not show any significant increase. 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, two different oxidation stability behaviors 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.

The hygroscopic property of methanol also effects the rate of oxidation. The water can induce faster ageing conditions.

7. Oxygen Consumption

The auto-oxidation is seen in 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).

Therefore, it is assumed that 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 calculations were done using he ideal gas equation as shown below in equation (2).

Experimental Duration	Fuel	O_2 consumed (mg)	O_2 consumed (%)	O_2 remaining in the reactor (mg)
24 hr	M15 Gasoline B	585.77	100.00%	0
48 hr	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 hr	Gasoline A	560	92.8	43.4
	Gasolne 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 1: Oxygen Consumption of fuels with respect to their ageing periods

$$PV = nRT \quad (2)$$

P = Pressure (Pa); V = Volume (m3); n = amount of gas (mol);

R = Universal gas constant (m3.Pa.K-1.mol-1); T = Temperature (K)

The oxygen consumption for each fuel is listed with respect to their experimental durations in the Table 1. 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. By analyzing and comparing the oxygen consumption for each fuel, it is 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 of gasoline B and M15 gasoline B is nearly equal which is 95 %-100 % (560 mg-600 mg).

From the observations, 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.

To calculate the amount of oxygen, two assumptions are made, 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.

Methanol has no effect on oxygen consumption in blends, but the stability of the blends 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, the oxygen consumption is independent of time durations of BigOxy accelerated ageing experiment. Also, 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. This could also indicate that the reduction in stability is mainly due to water.

8. Results of PetroOxy Oxidation Stability

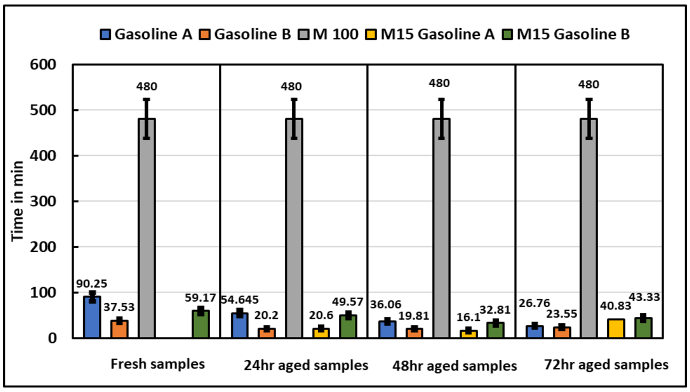

Figure 11: Results of PetroOxy Oxidation Stability

The graph in the Figure 11 shows the oxidation stability (min) of the fuel samples for the petroOxy ageing tests conducted to the fresh and BigOxy aged samples. 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 sample is tested.

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

Since pure methanol was very stable throughout all the ageing experiments, the oxidation stability of the 24 h aged methanol sample was >8 h. Therefore, in the Figure 11 it is shown as 480 min (8 h).

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. For fresh M15 gasoline A, the pressure exceeded 18 bar and the device was automatically switched off. But, the M15 gasoline A has the oxidation stability higher than M15 gasoline B. For the PetroOxy results of BigOxy aged M15 gasoline A samples, the oxidation stability has reduced with the range of 16 min-40 min.

For M15 gasoline B. The fresh sample has highest oxidation stability compared to aged samples. The PetroOxy oxidation stability for aged samples have decreased slightly as the BigOxy ageing duration increased.

From the observation of these results, it is evident that the fuel degradation increases with respect to their ageing time. This indicates the PetroOxy oxidation stability decreases as the BigOxy ageing duration increases.

9. Results of Water Content

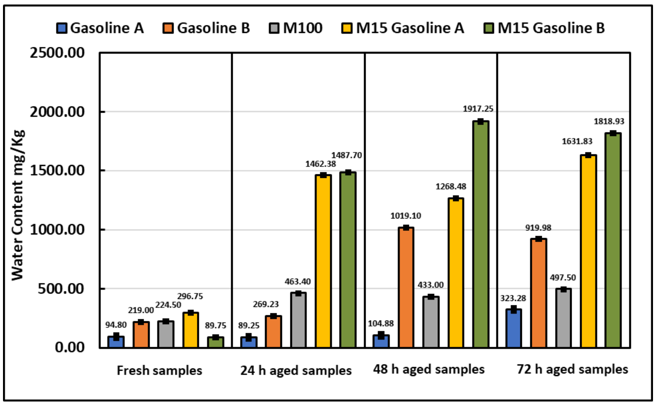

Figure 12: Water Content of the Fuels

After the hydroperoxide (ROOH) radical decomposes, it forms alkoxy (RO•) and hydroxyl radical (OH•) as seen in reaction (3) below. The hydroxyl radical further reacts with fuel and forms water as seen in reaction (4). 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.

$$ROOH \rightarrow RO \bullet + \bullet OH \qquad (3)$$

$$\bullet OH + RH \rightarrow H_2O + R \bullet \qquad (4)$$

As seen in the Figure 12, the graph shows the water content (WC) (mg/Kg) of the all the fuel samples with respect to their ageing period along with fresh samples. 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). The maximum increase when the fuel approaches its induction period (63 h) is observed. This indicates the propagation reaction happened in 72 h experiment. Gasoline A has the highest induction period out of all fuels used which showed pressure drop. One of the possible reasons might be, because of the water content in fresh gasoline A itself is very low compared to others. The WC of 48 h aged gasoline B is significantly higher than the 24hr aged and fresh sample (increased from 269.23 mg/Kg-1019.10 mg/Kg). The 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.

As the induction period of M15 gasoline A is 31 h, the propagation reaction happens at 48 h experiment. Therefore, if compared, 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 M15 gasoline A is in the range of 1200 mg/Kg-1600 mg/Kg.

The WC of 24hr 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 sample in in the same 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 due to the highest water content in fresh sample itself.

By this observation of increasing water content with respect to time, 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 time of the fuels. The significant increase (max increase in the WC) is found in 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.

10. Results of Acid Content

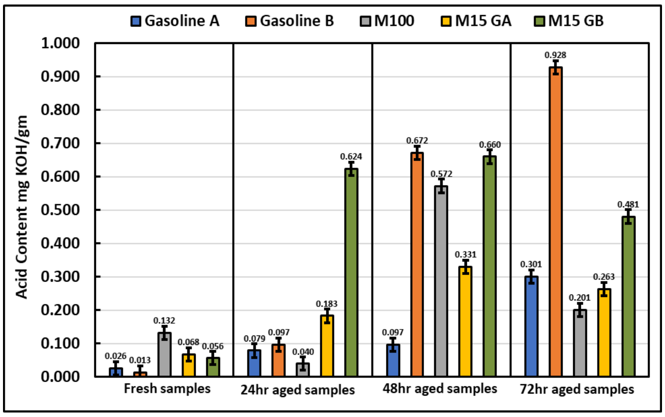

Figure 13: Acid Content of the fuels

The alkoxy radicals form acids, aldehydes and ketones by separation of hydrogen after reacting with fuels as seen in below reaction (6).

$$ROOH \rightarrow RO\bullet + \bullet OH \quad (5)$$

$$RO\bullet + RH \rightarrow ROH + R\bullet \quad (6)$$

From the graph shown in the Figure 13, 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 is in the range of 0.07 mg KOH/gm-0.09 mg KOH/gm with a slight increase in 48 h from 24 h.

Similarly, the 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).

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 it is a stable molecule.

The AC 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 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, the propagation reaction has happened in the 24 h experiment resulting in the maximum increase of acid content (AC). The AC of 48 h and 72 h experiments are not that different, which is in 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. This indicates that the oxidation stability of the fuel decreases as the AC increases. 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 rage of 0.04 mg KOH/gm – 0.5 mg KOH/gm throughout the experiments. This validates the stable behavior of methanol towards long term storage with respect to oxidation stability as an e-fuel.

11. Conclusions

The BigOxy method with 5bar 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. By observing their results for oxidation stability, 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. E-fuel which is Methanol (M100) that is used in the BigOxy experiment did not show any ageing phenomenon and was stable throughout the 24 h, 48 h and 72 h experiments. Therefore, the properties of pure methanol make it highly stable fuel in terms of oxidation stability for accelerated ageing methods.

Speaking of the analytical tests that were conducted, the quality of oxidation stability is not only the capacity of the fuel to resist the autooxidation 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 very stable in every experiment conducted for ageing and even analytics.

Therefore, it is evident that the BigOxy accelerated ageing method is compatible for Methanol, Gasoline and their 15% methanol blends. The reproducibility of the results is good. The analytical test results for water content and acid content furthermore validates the application of this ageing method.

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