

Oxidation of Methanol using different oxidizing agents for the synthesis of Formic Acid, and its reactor design



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Dedication

This work is dedicated to Mr. Abdul Sattar Edhi, Chairman Edhi Foundation, for his countless and lifelong services to mankind. His selfless services, irrespective of the religion and region, have played a very important role in transforming the society in to a better one. He has set an example by honestly using charity money, and has thus changed the attitude of the Pakistani nation towards charity, which now stands as the most charitable nation of the world. No award can honor his services, and this dedication is just to show our gratitude and love for Mr. Abdul Sattar Edhi. May Allah bless him with health.

DANIYAL HASAN

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Abstract

Formic acid is the simplest, single carbon atom, carboxylic acid. It is widely used in textile industry and leather tanning industry, for its characteristics of giving best finishing of the dye. Due to the low indigenous production of the Formic Acid in Pakistan, a considerable quantity is being imported which causes a burden on the exchequer. Various production routes are currently used for the production of Formic Acid; however, currently used methods have associated problems. Conversion of alcohols to their respective carboxylic acids is precedent in literature, so the oxidation of methanol to formic acid was investigated. To make the reaction energy efficient, Ultraviolet light was used as a source of energy. Commonly used oxidizing agents, including citric acid, potassium dichromate, potassium permanganate and hydrogen peroxide were tested for the formation of formic acid. High Performance Liquid Chromatography coupled with ultraviolet detector was used for the analysis of the samples. It was observed that except hydrogen peroxide, other oxidizing agents did not give any considerable formation of Formic Acid. Molybdenum oxide was used as a catalyst along with Hydrogen peroxide, to accelerate the dissociation of hydrogen peroxide into hydroxyl radical and hence increase the rate of reaction under ultraviolet light. Results showed that process provided considerable conversion of Formic Acid with 85% efficiency. Reaction kinetics was established and a batch reactor was designed on Aspen Plus for the synthesis of Formic Acid.

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Chapter

1 Background and introduction

1.1 Background

Formic acid is a largely produced industrial chemical, owing to its very wide range of applications especially in textile industry and leather tanning industry. Textile industry and leather industry constitute the back bone of the Pakistan's exports, but there is no indigenous production of formic acid. Formic acid is totally imported in Pakistan which creates the problems of increasing burden of import bills on exchequer, delay in supply of orders and heavy import duties.

A simple and cost effective route for the production of formic acid can be very beneficial to the industry [1]. Oxidation of methanol, simplest alcohol, to Formic acid is literally the simplest possible route [2]. To achieve this conversion in the most economical way, efficiency of various commonly used economical oxidizing agents will be tested. Use of ultraviolet light is becoming popular for its added advantages compared to high pressure and high temperature reactions. Ultraviolet light will be incorporated in the reaction setup to check its feasibility for the conversion of methanol to formic acid. There are some photoactive catalysts which activate under ultraviolet light and facilitate photochemical reactions. Efficiency of catalytic and non-catalytic reactions will be compared and based on their results; a reactor will be designed for the synthesis of formic acid.

1.2 Formic Acid

Formic acid is the first member of the carboxylic acid family (compounds with -COOH functional group). Formic acid derives its name from Latin word "Formica" which refers to ant. It occurs naturally in the venom of the ant and also artificially manufactured. It has its major application in textile industry. It is also called methanoic acid. Its chemical formula is HCOOH .

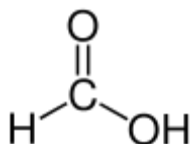


Figure 1-1: Structure of Formic Acid

Formic acid is a colorless, fuming liquid with a pungent odor. Its fumes cause irritation in breathing and can damage skin. It freezes at 8.4 °C (47.1 °F) and boils at 100.7 °C (213.3 °F). Due to presence of both carboxylic and aldehyde group, it has both properties of an acid and reducing agent. However formic acid is not a typical carboxylic acid; it is unique in its strength as an acid, its inability to form anhydride and its reducing property (like an aldehyde) [3]. It is miscible with water, alcohol and ether in all proportions [4].

1.2.1 Physical Properties

Table 1-1: Physical properties of formic acid

Physical Property	Characteristic behavior
Molecular Weight	46.02538 g/mol
Molecular Formula	CH ₂ O ₂
Color	Colorless fuming liquid
Odor	Pungent, penetrating odor
Taste	Sour
Boiling point	101°C
Melting point	8.3°C
Flash point	156°F(closed cup) 138°F (open cup)
Solubility	Miscible with ether, acetone, ethyl acetate, methanol, ethanol; partially soluble in benzene, toluene, xylenes Miscible with water Solubility 1000000 mg/L (at 25°C) [5]
Density	1.220 at 20°C/4°C Vapor Density 1.59 (Air = 1)

Vapor Pressure	42.59 mm Hg at 25°C
Stability	May deteriorate in normal storage and cause hazard.
Auto ignition	1004 °F (539 °C); 90% solution: 813 °F (434 °C)
Decomposition	At high concentrations, of 98-100%, formic acid slowly decomposes and carbon monoxide is liberated which can lead to rupture of the sealed glass containers. In absence of gas leakage, a full 2.5 L bottle would develop a pressure of over 7 bar during 1 yr at 25 °C. [6]
Viscosity	1.607 mPa.s at 25°C
Surface Tension	37.13 mN/m at 25°C
Ionicity	11.05 eV
Relative Evaporation Rate	2.1 (Butyl acetate = 1)

1.2.2 Chemical Properties

Table 1-2: Chemical properties of Formic Acid

Chemical Property	Characteristic behavior
Heat of Fusion	12.68 kJ/mol
Heat capacity	2.151 J/g-K at 25°C
May act both as an acid and as an aldehyde because the carboxyl is bound to a hydrogen rather than an alkyl group	
Strong reducing agent	
Ionization potential	11.33 eV
Heat of formation	-425.0 kJ/mol
Henry's Law constant	1.67×10^{-7} atm-m ³ /mol at 25°C
Hydroxyl radical reaction rate constant	4.50×10^{-13} cm ³ /molecule-sec at 25°C

pKa	3.75 (at 25°C)
Dissociation Constants	pKa = 3.75 at 20°C
Corrosivity	Corrosive to metals
Heat of combustion	254.6 kJ/mol at 25°C (liquid)
Heat of vaporization	20.10 kJ/mol at 25°C
Log P	log Kow = -0.54

1.2.3 Spectral Properties

Table 1-3: Spectral Properties of Formic Acid

Spectral Property	Formic acid characteristic
Max Absorption	(Undiluted): 256 nm (Epsilon= 165)
Index of refraction	1.3714 at 20 deg C/D
IR	15 (Sadtler Research Laboratories IR Grating Collection)
¹ H NMR	6653 (Sadtler Research Laboratories Spectral Collection)

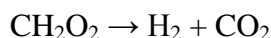
1.2.4 Uses of Formic Acid

Formic Acid has very wide and diverse applications and advantages:

- Formic acid is used in textile industry to control pH by neutralizing sodium hydroxide; this has direct effect on dyeing efficiency. To achieve the same results the amount of formic acid required is only one third of the amount required of acetic acid or citric acid.
- Formic acid is used in leather tanning and dye fixing, for its acidic properties, as masking agent for chrome tanning baths.
- Formic acid has very low environmental impacts, as it is biodegradable and its Chemical Oxygen Demand (COD), which is the oxygen required for degradation, is very low. Thus the effluent has less impact on the eco system and less rigorous effluent treatment is required.
- Formic acid is used in oil field applications to dissolve calcium carbonate.

- Formic acid can be used for descaling in industrial as well as domestic uses.
- Formic acid is used in electroplating as an acid-metal cleaner and oxide remover.
- Formic acid serves as a coagulant in rubber manufacturing industry.
- Formic acid, along with hydrogen peroxide, is used as an oxidizing agent for the manufacturing of epoxidized soya bean oil.
- Formic acid can be used as a material of hydrogen storage [7, 8]. Catalytic decomposition of formic acid, in the presence of platinum, produces hydrogen and carbon dioxide [9]. Formic acid can store almost 3.5 times hydrogen as compared to compressed hydrogen gas. At room temperature formic acid has 53g/L hydrogen while compressed gas has 14.7 g/L hydrogen at pressure as high as 350 bar.

The reaction is



- Derivative of formic acid (Salts) are used to increase the grip of road during snowfall and rain. For example Potassium Formate; a salt of formic acid, is used for deicing on roads and airport runways. Beside the efficiency, formic acid has an extra advantage of being biodegradable.
- Agriculture industry utilizes formic acid as an antibacterial preservative, pesticide, food additive and additive to animal feed and silage.
- Formic acid has dual function when used with silage, it provides antibacterial support and favors low temperature fermentation of silage thereby lowering the overall time and increasing the nutritional value. [10]
- Some active pharmaceutical ingredients are synthesized from formic acid.
- Formic acid is effective against disease of “Warts” and it has also been marketed by some pharmaceutical companies.
- Formic acid can kill E.Coli bacteria, for this property it is added to poultry feed. [11]

1.3 Methanol

Methanol is the simplest, single carbon, alcohol. It is also named as methyl alcohol or wood alcohol. Its chemical formula is CH₃OH.

It is highly volatile, low boiling liquid. Unlike ethanol it is a toxic chemical and used for poisoning ethanol and making it unfit for drinking. It is largely used as a solvent, anti-freeze agent and fuel as well [12].

Methanol is also reported to be produced from carbon dioxide using catalyst in the presence of sunlight, thus imbalance of the CO₂ in the atmosphere can also be controlled by converting CO₂ to methanol and subsequently utilizing it for industrial uses.

1.3.1 Physical and Chemical Properties

Table 1-4: Physical and Chemical properties of Methanol

Property	Characteristic behavior
Color	Colorless
Solubility	Miscible with ethanol, ether, benzene, acetone, chloroform, most organic solvents and ketones. Miscible in water at 20°C
Odor	Alcoholic pungent odor
Boiling Point	64.7°C at 760 mm Hg
Melting Point	-97.8°C
Flash Point	15.6 °C (open cup) 11.0°C (closed cup)
LogP	log Kow = -0.77
Auto-Ignition	867°F (464°C)
Decomposition	Decomposition results in emission of acrid smoke and irritating fumes.
Viscosity	0.544 mPa sec (at 25°C)
Heat of Combustion	726.1 kJ/mole
Heat of Vaporization	37.34 kJ/mole (at 25°C)
Surface Tension	22.07 mN/m (at 25°C)
Ionicity	10.84 eV
Dissociation Constants	pKa = 15.3

1.3.2 Uses of methanol

Methanol is a highly useful chemical.

- It is used for denaturing ethanol.
- It can be directly used in internal combustion engines.
- It is used as a solvent for its polar nature.
- It is used for producing biodiesel [12].
- It is used as a fuel in Direct Methanol Fuel Cells [12].
- It is used as an anti-freeze agent in the radiators of the vehicles. [13]
- For its flammable properties, it is used as a fuel in camping stoves.
- It is the starting material of various polymers.
- It is used as a solvent in High performance Liquid Chromatography for its spectroscopic properties.
- It is used in waste water treatment, where it serves a feed to bacteria which convert dangerous compounds of nitrates to nitrogen gas.
- It is widely used as a raw material for producing various industrial chemicals including chlorofluoro carbons, acetic acid, methyl mercaptans, methylamines, methyl acrylates etc. [14]

Chapter

2 Literature Review

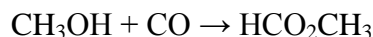
2.1 Formic Acid synthesis routes

Formic acid is currently produced using various methods. These methods have either complex route or they have associated problems of availability of raw materials, low yield and disposal of by-products.

2.1.1 Formic acid from methyl formate and formamide

Reaction of methanol and carbon monoxide under a strongly basic environment results in the formation of methyl-formate. Methyl-formate is then hydrolyzed to form formic acid.

Chemical reaction is [15]



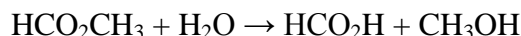
It is a liquid phase reaction carried out at 80 °C and 40 atm.

Capturing carbon monoxide and its separation from the gas mixture is a costly and difficult step. Carbon monoxide is a highly poisonous gas, so its handling is also very critical. Reaction is a high temperature, high pressure reaction; the equipment made of high grade material is required for such a reaction.

2.1.2 Formic acid from methyl formate

Formic acid can be derived from methyl formate by hydrolysis.

The reaction is [16]

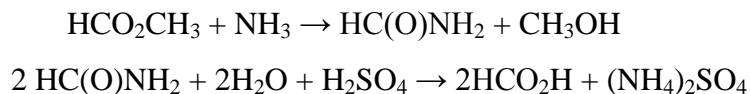


This requires a large amount of water and supply of methyl formate is itself a problem.

2.1.3 Formic Acid from Formamide

Formic acid can also be derived from methyl formate by reacting it with ammonia forming formamide, followed by hydrolysis in the presence of sulfuric acid.

The reactions are [16]



Beside the requirement of large amount of water and supply of methyl formate, disposal of ammonium sulfate also possess a major problem. This is a multi-step process whose efficiency decreases with every step.

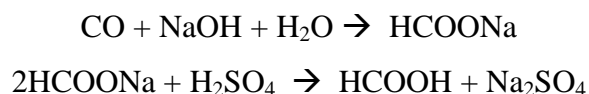
2.1.4 Formic acid as by-product of acetic acid production

Initially Acetic acid was synthesized by oxidation of alkanes, formic acid was a by-product of this reaction [17, 18]. Use of formic acid was first investigated during 1960s when significant amount of formic acid was produced as a by-product of acetic acid. Now the requirement of formic acid has increased enormously so the production of formic acid achieved as a by-product of acetic acid is not enough to fulfill the required quantity.

2.1.5 Formic acid from carbon monoxide

Carbon monoxide when reacted with sodium hydroxide then sodium formate is produced which is then converted to formic acid by the action of sulfuric acid. Reaction of carbon monoxide and alcohol (e.g. methanol) yields respective esters of formic acid.

The chemical reaction is [18]

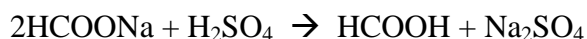


Capturing and separating carbon monoxide is a difficult process. Owing to the poisonous nature of the carbon monoxide, the handling and recovery of unreacted carbon monoxide is a potential health hazard.

2.1.6 Formic acid by reaction of sodium formate and sulfuric acid

Sodium formate can be converted to formic acid, by reacting it with sulfuric acid. [18]

The reaction is



The production of sodium formate at such a large scale is itself a problem while the disposals of sodium sulfate salt also possess a problem.

2.1.7 Formic acid by hydrogenation of carbon dioxide

Catalytic hydrogenation of CO₂ can produce formic acid and this route has long been investigated [19]. This process can be significant to remove the accumulating carbon dioxide in the atmosphere; however the efficiency of this process is still not good enough to be adopted at industrial scale.

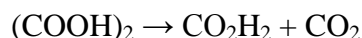
2.1.8 Formic acid by oxidation of biomass

OxFA process produces formic acid from biomass by aqueous phase partial oxidation; CO₂ is produced as a by-product. Biomass includes sugars, wood, waste paper and likes. Commonly used catalyst is Keggin-type polyoxometalate (H₅PV₂Mo₁₀O₄₀) [20, 21]. Growing biomass requires a large area and it is a slow process so meeting the growing demand of formic acid using this process will be a tough task.

2.1.9 Formic acid from oxalic acid

Oxalic acid {(COOH)₂ or C₂O₄H₂} when heated in the presence of glycerol {C₃H₈O₃} which acts as a catalyst then formic acid is produced. Overheating can result in the formation of allyl-alcohol {CH₂=CHCH₂OH}.

The chemical reaction is



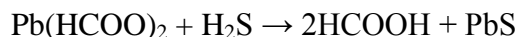
Formic acid is then extracted from the mixture by steam distillation [22].

This method is used at laboratory scale and has not been scaled up to industrial level.

2.1.10 By reaction of lead formate and hydrogen sulphide

Reaction of lead formate {Pb(HCOO)₂} and hydrogen sulfide {H₂S} produces formic acid and lead sulfide as a by-product. [23]

The reaction is



This method is used at lab scale. Handling lead compounds at a large scale and their disposal has various environmental regulations on it.

2.1.11 Biosynthesis of formic acid

Formic acid occurs widely in nature as its conjugate base formate. Conjugate base formate is produced by enzymatic reduction of carbon dioxide {CO₂} where enzyme used is “Formate dehydrogenase” [24].

This reaction is environmentally very useful as it reduces carbon dioxide in the atmosphere and does not produce any dangerous chemical as a by-product. However meeting the industrial demands by using slow bio-reactions is a difficult task.

2.2 Carboxylic acids from alcohols

Principally the oxidation of alcohol should yield aldehydes, carboxylic acid or ketones, depending upon the position of the hydroxyl group. The oxygen atoms will attach to the

carbon atom attached to the hydroxyl group as the carbon atom has a partial positive charge on it and will tend to further stabilize itself. If the alcoholic group is on the terminal carbon atom then it is called primary alcohol while compounds having alcoholic groups on non-terminal carbon atoms are called secondary alcohols. Oxidation of primary alcohols first yields aldehydes and then further oxidation yields carboxylic acids. Secondary alcohols oxidize to ketones. [25]

Carboxylic acids are produced by oxidation of respective primary alcohols. This oxidation can be carried out at low temperatures by using ultraviolet light; in that case some catalyst with photochemical properties is used. Ultraviolet light provides energy required for the chemical transition while photo-catalyst promotes the absorption of energy and thus promotes the rate of reaction.

Zhao, M., et al have reported the conversion of primary alcohols to respective carboxylic acid where they tried the performance of various catalysts [26, 27]; however, this particular conversion of methanol to formic acid is not reported in literature.

2.3 Metabolism of Methanol to Formic Acid

When methanol enters the body of a living organism, it gets converted to formic acid. Formic acid has various adverse effects on the body and might result in blindness or even death, this is called methanol poisoning. The conversion of methanol to formic acid is by metabolic reaction [15]. Alcohol dehydrogenase brings about this metabolism [28].

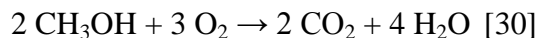
It gives a possibility of industrially producing formic acid by oxidation of methanol. To achieve the oxidation of methanol to formic acid on an industrial scale either enzymatic action is required or we can design a reaction setup which could reciprocate the catalytic action of the alcohol dehydrogenase.

2.4 Electro catalysis of methanol to Formic Acid

Oxidation of methanol has been facilitated by electrolysis combined with the use of catalyst. The catalyst should have the property of breaking Carbon-Hydrogen bond, this property is best shown by Platinum. Methanol is oxidized to carbon dioxide and formic acid using the process of electrolysis in which catalyst coated electrodes are employed [29].

2.5 Oxidation of methanol in nature

Methanol is a naturally degradable compound. It reacts with atmospheric oxygen under the influence of sunlight and gets oxidized.



Sunlight has a wide spectrum of light. The light rays with the wavelength falling in the ultraviolet range are absorbed by methanol and it gets degraded to carbon dioxide and water, this takes a time of about 3-4 days.

Reciprocating the other conditions and by limiting the time of reaction there is a possibility to achieve a controlled oxidation of methanol to formic acid.

2.6 Photolytic chemical reactions

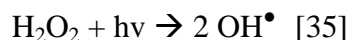
Ultraviolet light consists of high energy waves. In chemistry, the energy of these waves is used for photoluminescence and this energy has also been used to carry out chemical reactions. The light is absorbed by the electrons which get promoted to the higher unstable orbitals, the excitation of electrons result in the formation of transition state complexes. Transition state complex is the high energy state where a complex is formed between reactants, the products are formed when the transition complex dissociates. Use of ultraviolet light has an advantage that the reaction can be carried out at low temperature and the energy is absorbed directly by the molecules, the waste of energy as specific heat and latent heat is avoided.

Ultraviolet light has been reported to be used to carry out various chemical reactions, especially organic oxidations. Vosooghian, H. et al have carried out oxidation of organic sulfides by combined effect of ultraviolet light and Titanium oxide, which is a renowned photocatalyst [31]. Similarly Wang et al have used ultraviolet energy for the destruction of humic acid in water [32]. Through their work Montaser Y.G., et al have shown that the oxidation of para-chlorophenol was improved and accelerated by the use of ultraviolet light in the reaction setup [33].

2.7 Wavelength of Ultraviolet light

Ultraviolet rays are electromagnetic waves with a wavelength ranging from 10nm-400nm. According to Plank's law shorter the wavelength higher is the energy of the rays. In organic chemistry, only two wavelengths of Ultraviolet light are generally used i.e. 365nm and 254nm. 365nm light is used for spectroscopic applications while high energy 254nm

ultraviolet light is used for organic reactions [34]. Ultraviolet light energizes the carbon-carbon bonds of the organic molecules, but this effect is only pronounced in unsaturated bonds. Carbon-oxygen bonds are not affected by ultraviolet light with a wavelength more than 160nm; this is the reason why alcohols are used as mobile phase for ultraviolet detection in characterization techniques. However ultraviolet light ionizes hydrogen peroxide and produces hydroxyl radicals. These radicals are highly unstable and react with the neighboring molecules thus bringing about the oxidation of organic molecules.



In the light of above mentioned literature, experimental setup was designed. It was opted to carry out the incomplete oxidation of methanol for achieving Formic acid; incomplete oxidation can be achieved by limiting the time of reaction. The low temperature, liquid state reaction will be energized by ultraviolet light. The ultraviolet light with wavelength of 254nm was used.

Chapter

3 Experimentation and Characterization Techniques

3.1 Characterization Method

A characterization method was necessary for the quantitative and qualitative analysis of the samples of the reaction mixtures. All the four main possible constituents of the reaction mixture i.e. Methanol, Formic acid, Formaldehyde and Water are colorless and miscible liquids which are difficult to recognize in a mixture. Both High Performance Liquid Chromatography (HPLC) and Gas Chromatography (GC) can be used for the analysis of the reaction mixture [36]. However, due to the availability, only High Performance Liquid Chromatography (HPLC) was used.

3.1.1 HPLC

High Performance Liquid Chromatography (HPLC) is a separation technique used to separate otherwise miscible constituents. It has a packed column over which constituents are separated, under high pressure, based on their retention time on the column which is then based on the interaction of the column and the constituent.

HPLC column are of two types

- a) Reverse Phase
- b) Normal Phase

Reverse Phase system has a non-polar stationary phase over which polar solvents are used as mobile phase; it is generally used for separation of polar species. [37]

Normal Phase system has a polar stationary phase over which non-polar solvents are used as mobile phase; it is generally used for separation of non-polar species. [38]

A detection system is coupled with HPLC to detect and quantify the constituents.

3.1.1.1 Method development

For the HPLC analysis of a particular mixture, a specified system is to be developed. Developing a system for analysis is a function of the constituents of the analyte. System development includes the following steps:

- Selection of the stationary phase
- Selection of a compatible mobile phase
- Dimensions of the stationary phase column
- Wavelength of Ultraviolet Rays for detection
- Flow rate of the solvent over the column

3.1.1.2 *Constituents of analyte*

Reaction mixture included formic acid, water, partly oxidized formaldehyde and unreacted methanol.

The method for analysis was developed based on the constituents of our analyte, keeping in mind the separation of all the species on the column and their clear identification.

3.1.1.3 *Stationary Phase/Column*

Reverse Phase C-18 column was used. This C-18 column is the most common of all and is efficient for separation of polar species. [39]

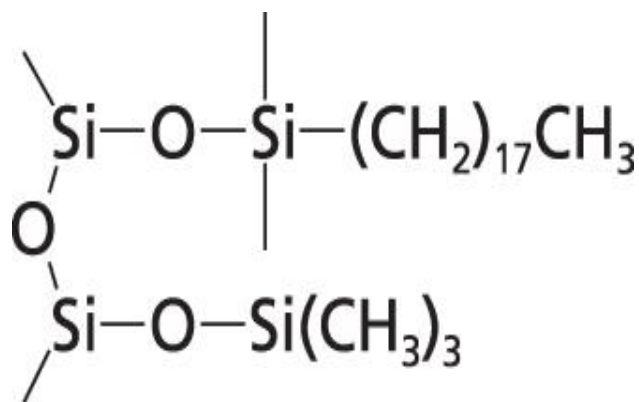


Figure 3-1: Structure of C-18 column

3.1.1.4 *Mobile Phase*

Methanol, Acetonitrile, Water or any of their combination is generally reported to be compatible with Reverse Phase C-18 column, however other mobile phases can also be used [40].

Acetonitrile, Water, Methanol and 50-50% mixture of Acetonitrile and Water were tested for the required analysis.

100% HPLC grade water was selected as a mobile phase because it gave the required results for the chemical of interest i.e. formic acid.

3.1.1.5 Column length

Length of the column is very critical for the separation of the species. Two column lengths of 10 cm and 25 cm were tested.

10 cm column gave a low retention time for formic acid i.e. less than 1 min and it also gave unsatisfactory separation i.e. overlapping peaks. Peaks before 1 min are also not considered credible.

25 cm column was selected because it gave better separation and delayed retention time for formic acid, thus excluding the early peaks given with 10 cm column.

Dimensions of the selected column were 25cm length and 5mm diameter.

3.1.1.6 Flow Rate

Flow rate of the mobile phase was adjusted to be 0.5ml/min as it gives clear peaks around a retention time of 4-5 minutes. Flow rate of 1.5ml/min gave peaks before 1 minute, as any peak before 1 minute is not recommended to be considered so the flow rate was decreased to 1ml/min. At flow rate of 1ml/min, although the peaks shifted in the time range of 3-4mins but the separation was not efficient and the peaks were partly overlapping. Flow rate was decreased to 0.5ml/min which gives clear separation and peaks in the time range of 4-5 minutes.

3.1.1.7 Standard Peaks

Water did not give any peak because it was used as mobile phase. Aldehydes have a characteristic property of forming di-ols when they come in contact with water, Formaldehyde thus forms di-ol. Due to the presence of the same functional group the peaks of di-ol (from formaldehyde) and methanol are very close. Formic acid, due to the distinct carboxylic group, gives a very distinct peak.

3.1.1.8 Wavelength

Methanol gives a maximum UV absorption at wavelength of 205nm while formic acid gives maximum absorption at 256nm. An intermediate value could have been selected to detect both the formic acid and methanol. However, both the compounds are polar compounds which show almost same retention time on C18 column [41]. It was also verified from the experimental results that both species give peaks around the same time of 4-5 minutes, so to avoid the confusion and overlapping of peaks, a wavelength of 250nm

was selected where Formic acid gives high absorption and gives sharp peaks while methanol does not give any peak at 250nm. Around 4-5 minutes there will be a peak of Formic acid while any other peak will be an impurity.

3.1.1.9 Methanol peak exclusion

Owing to the similarities in the chemical structure of Methanol and Formic Acid, standard solutions of Methanol and Formic Acid eluted at the same retention time i.e. 3-4 minutes. To avoid the confusion 250nm wavelength was selected to exclude the peak of methanol which was creating confusion. Results show that methanol shows a sharp peak at wavelength of 205nm (right side), while at wavelength of 250nm (left side) this peak disappears and becomes negligible (Figure 3.1-3.2).

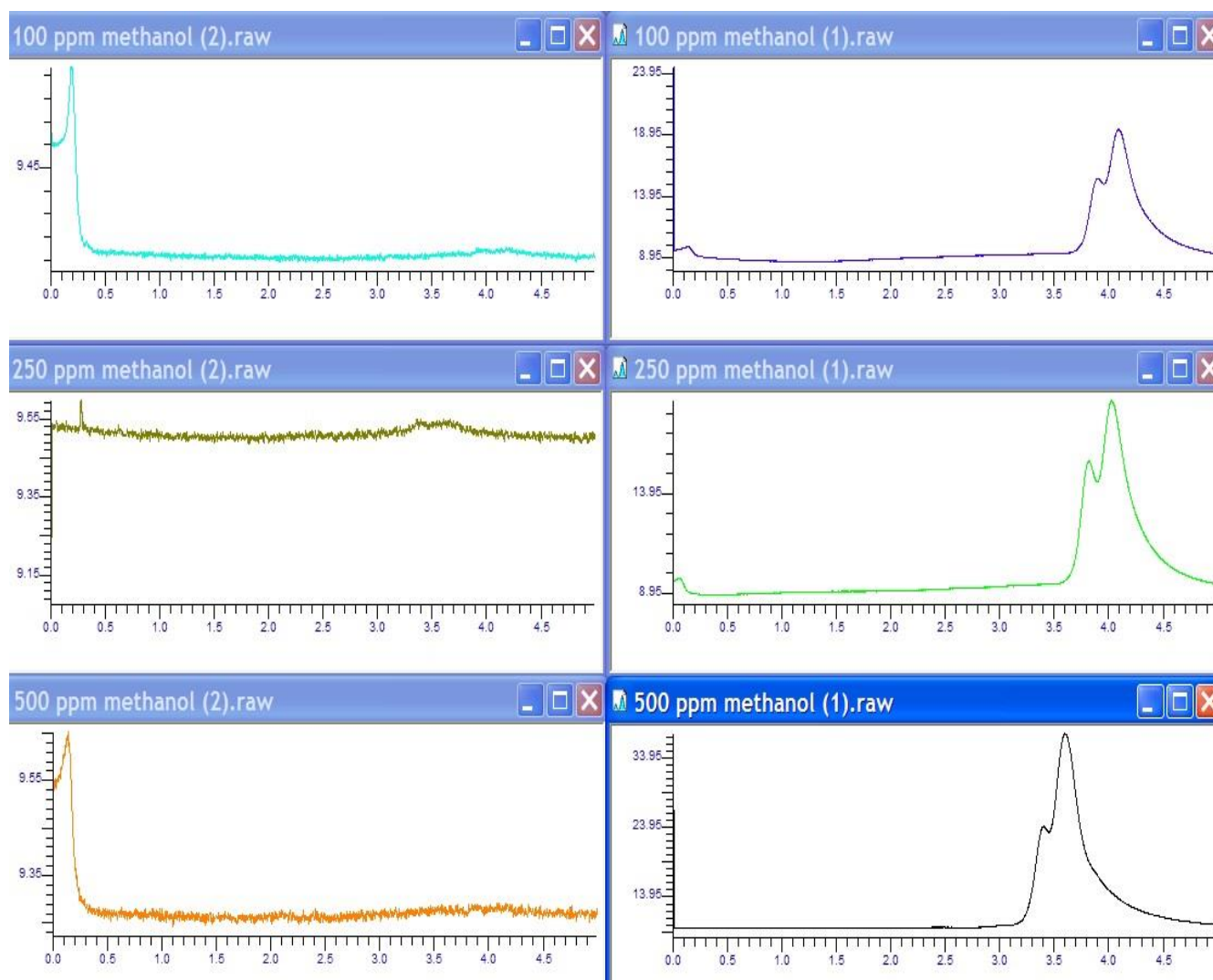


Figure 3-2: Comparison of HPLC peak of Methanol at 250nm Vs. 205nm

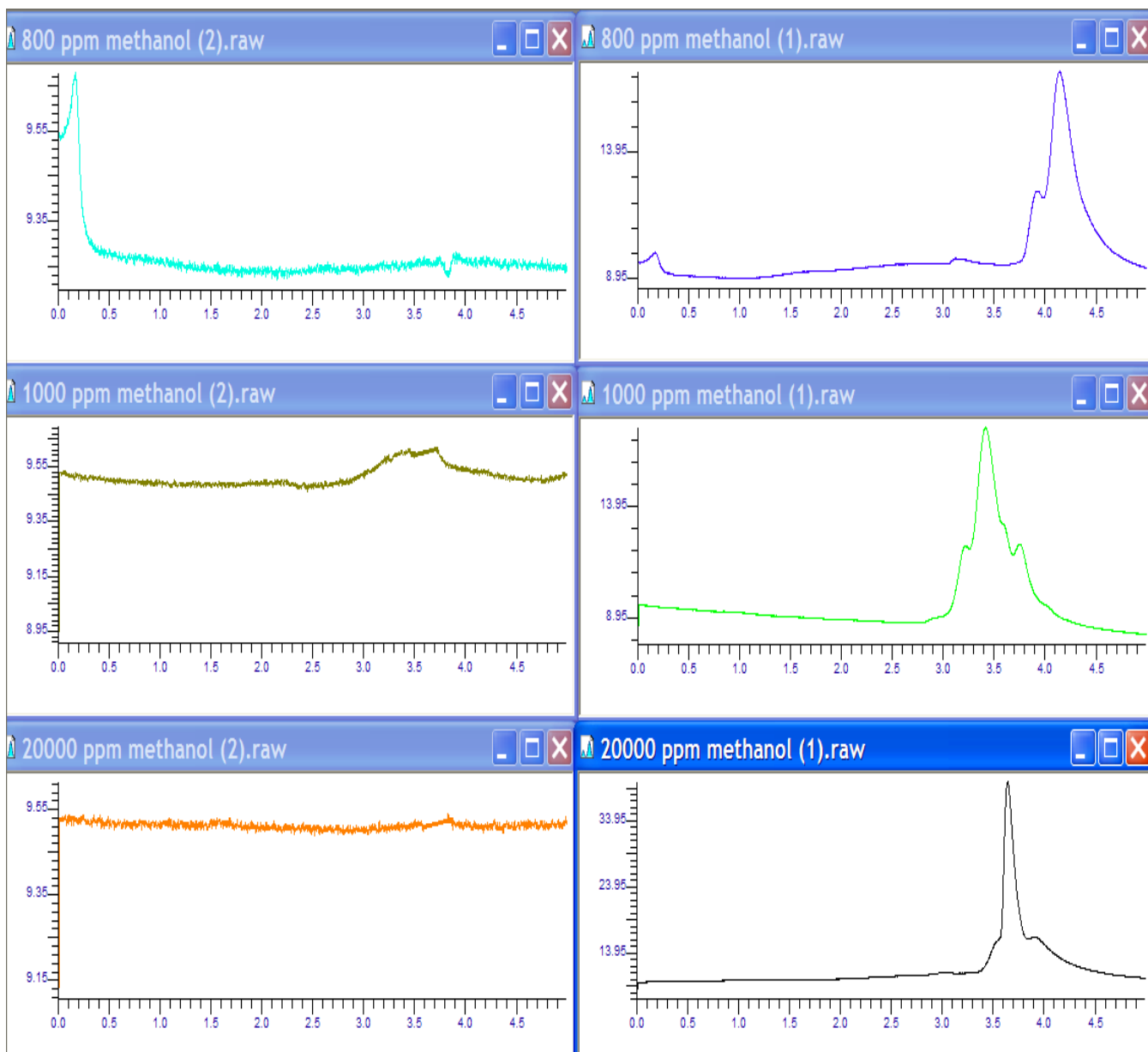


Figure 3-3: Comparison of HPLC peak of Methanol at 250nm Vs. 205nm

From the experimental results it was concluded that the only peak given by sample at 250nm wavelength shall be Formic Acid.

3.1.1.10 Formic Acid Calibration curve

The standard solutions of Formic Acid were prepared by diluting it in water, and then the area under the peak for each concentration was plotted to get a calibration curve.

The below chromatogram shows the absorption curve for 100% Formic Acid (Detailed chromatograms of each concentration attached in Annexure A)

Sample Name: formic acid 100% 21-10-2015

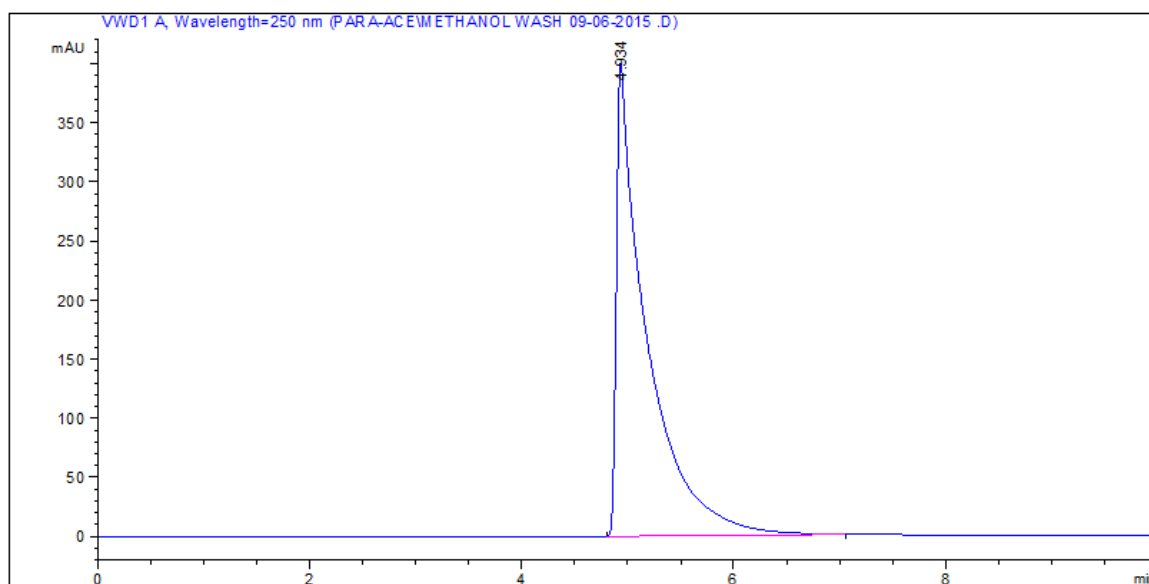


Figure 3-4: Chromatogram for 100% Formic Acid

Table shows the data of area under the absorption curve against each concentration.

Table 3-1: Formic Acid Concentration Vs. HPLC Absorbance

Concentration (%)	Area under curve (mAU*s)
1.25	318.02
2.5	492.71
5.0	855.29
10	1401.71
20	2419.25
30	3084.15
40	3869.84
50	4250.18
60	4826.22
70	5357.11
80	5971.99
100	7019.62

Figure shows the calibration curve for Formic Acid concentration, it plots the area under the absorption curve against each concentration.

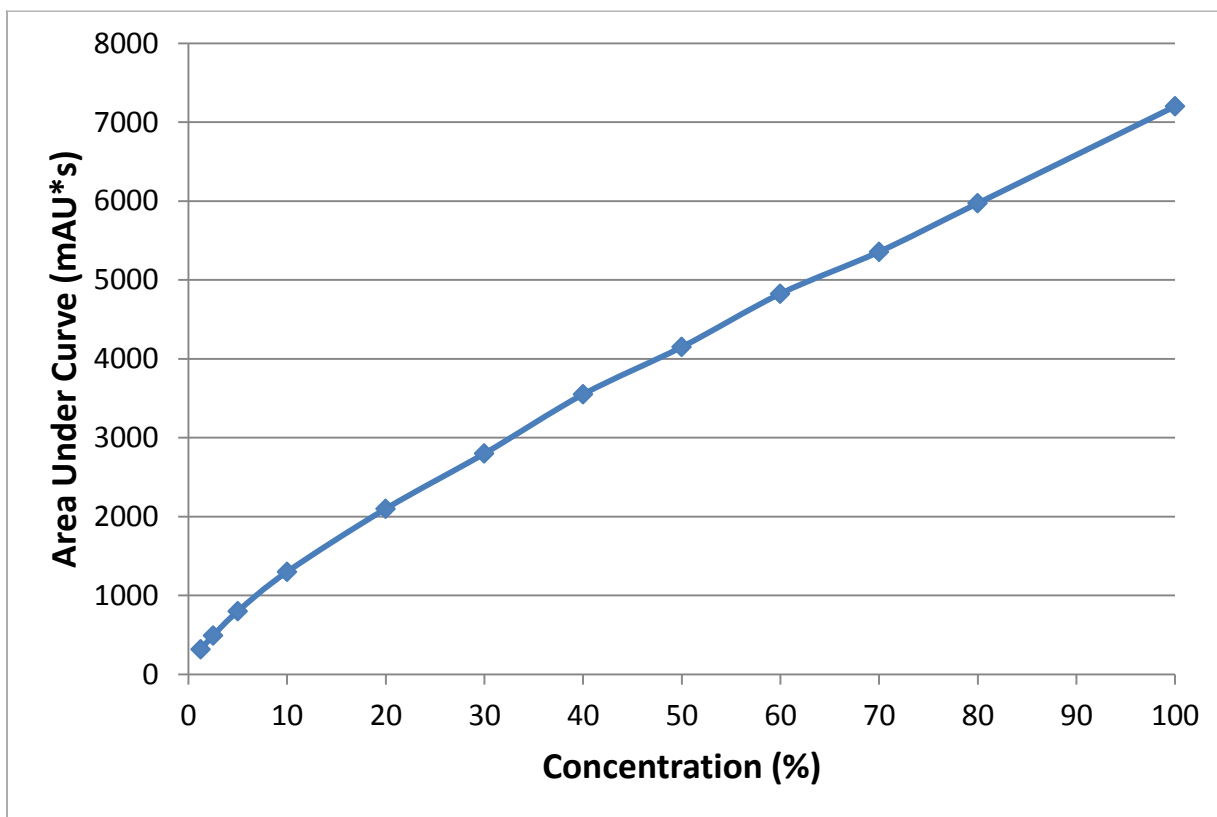


Figure 3-5: Calibration curve for Formic Acid concentration

3.2 Experimental setup

3.2.1 Phase of reaction

To carry out any chemical reaction, there needs to be the right balance of the reactants, having enough contact and the source of energy which will bring about the transition of chemical species. Methanol is the main reactant and it is a volatile compound while the product of interest, Formic Acid, is also a highly volatile compound. For volatile compounds, depending upon the phase, reactions are classified as:

- a) Gas Phase reactions
- b) Liquid Phase reactions

3.2.1.1 *Gas Phase Reactions*

In gas phase reactions the compounds change their phase from liquid to gas due to the temperature rising above their boiling point. To have a better contact of scattered gas molecules, tubular or plug flow reactors are generally used. These reactors are costly and also need downstream equipment for condensing the components. Gas handling is itself a critical activity.

3.2.1.2 *Liquid Phase Reactions*

Volatile compounds can also be reacted in liquid phase. There are two possibilities

- a) Reaction temperature is less than the boiling temperature and there is enough pressure on the liquid to avoid its evaporation.
- b) The compounds are dissolved in a solvent which improves the contact of reacting compounds and also absorb the heat and thus suppresses the evaporation.

Although both liquid phase and gas phase reaction setup could be used for this type of conversion but to keep the process simple, liquid phase reaction was adopted. This would decrease the energy required to change the phase of the liquid reactants to gaseous state, would not require downstream equipment to condense the product stream and would also simplify the contact pattern compared to the complex scheme for contact of reactants in gas phase.

3.3 **Experimental conditions**

To provide sufficient energy for chemical transition without increasing the temperature of the system, ultraviolet light was used as a source of energy. High energy ultraviolet light of wavelength 254nm was used, use of which is also precedent [34]. Electrons of the reacting components directly absorb energy and get excited; the molecule is then most likely to form a transition complex. The reactions were carried out at room temperature, which was recorded to be 27°C. The reactions were carried out atmospheric pressure. Glass beakers with closed lids were used to carry out the reaction, because glass material has the characteristic of high transmission of ultraviolet light and the closed lid would limit the escape of vapors from the system; after collision among themselves and with the walls of the beakers, the vapors lose their energy and condense back to liquid phase. Magnetic stirrers were used for stirring the reaction mixtures, stirring helped to achieve better contact

and homogeneity of the reaction mixture. A reaction time of 4 hours was given to each sample to ensure enough conversion of the reactants.

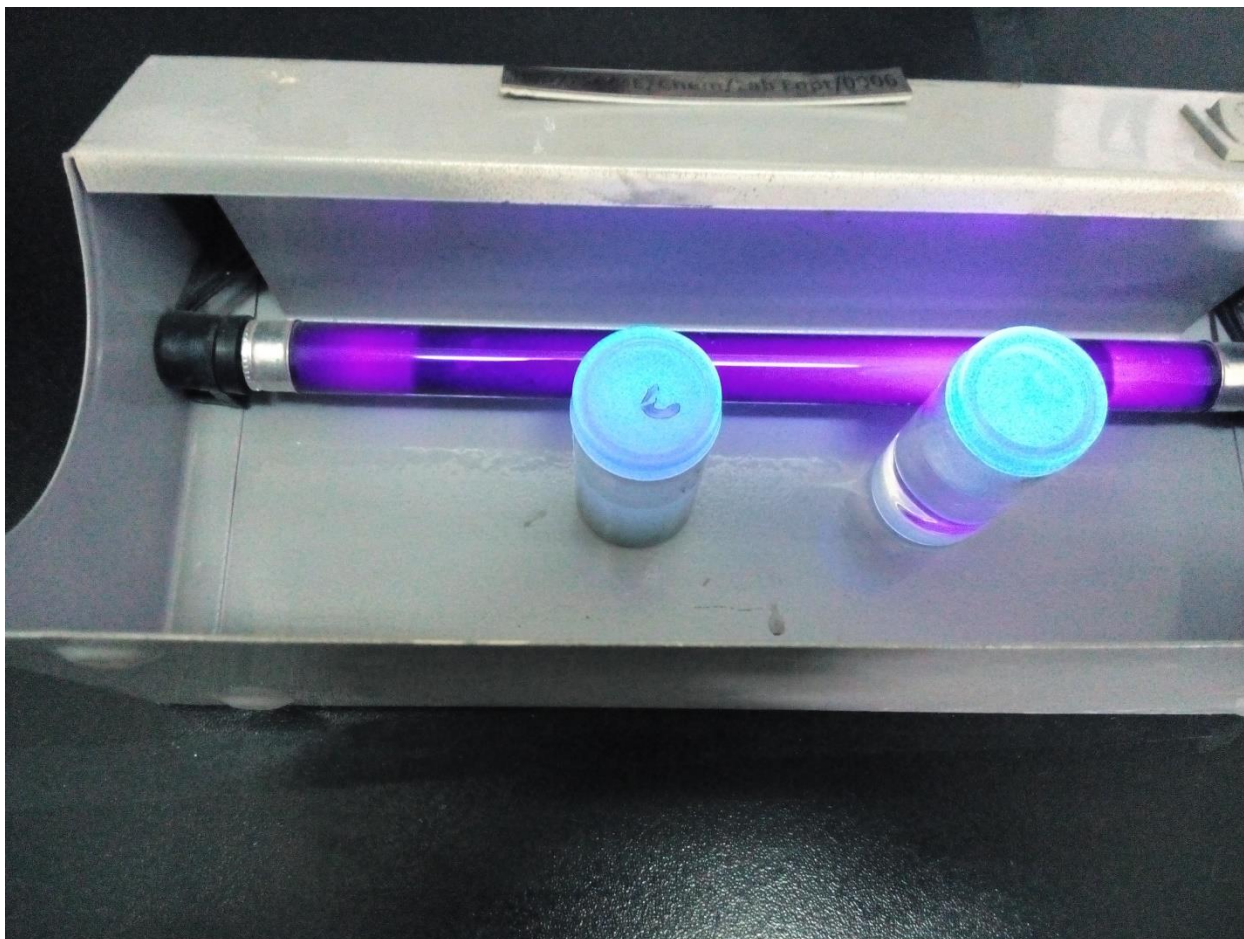


Figure 3-6: Experimental setup for reaction under UV-light

3.4 Oxidizing agents

Various oxidizing agents were to be tested. Role of the oxidizing agents is very critical because it will initiate the reaction. The following oxidizing agents were tested for their efficiency to carry out the oxidation of Methanol to Formic Acid under our reaction setup.

- a) Citric Acid
- b) Acidified Potassium dichromate
- c) Acidified Potassium permanganate
- d) Hydrogen peroxide

3.5 Materials

All the chemicals were of highest purity available including: Citric acid (VWR BDH); Potassium permanganate (Merck); Potassium dichromate (Merck); Sulfuric Acid (Sigma Aldrich); Hydrogen peroxide 50w/w percent (Sigma Aldrich); Methanol 95w/w percent (Sigma Aldrich); Formic Acid 94 w/w percent (Sigma Aldrich); HPLC grade water (Sigma Aldrich); Molybdenum oxide. All these chemicals were locally arranged through Musa Gee Chemicals Private Limited.

3.6 Experimentation

Experiments were carried out to test the performance of various commonly used oxidizing agents, under our reaction conditions. To test the relative performance, the reaction conditions were kept constant.

3.6.1 Oxidation of Methanol using Citric acid as oxidant

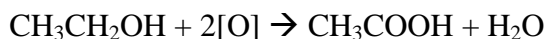
Citric acid (C₆H₈O₇) is a mild acid, found naturally in fruits. It facilitates metabolism where Methanol is converted to Formic Acid, hence it was tested as an oxidant.

1 Molar solution of citric acid was made by dissolving 19.22 gram of Citric acid in 100ml water. Three reaction assemblies were setup to test the performance of Citric acid under three different volume ratios. 4ml, 6ml and 10ml, of 1M Citric acid solution, were added in 10ml of methanol and a reaction time of 4hours was given. Stirring and irradiation by ultraviolet light continued for the entire reaction time. The reaction mixtures were then analyzed using high performance liquid chromatograph.

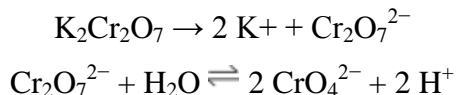
3.6.2 Oxidation of Methanol using acidified Potassium dichromate as oxidant

Potassium dichromate (K₂Cr₂O₇) is reported for its use for oxidation of compounds. It has a molar mass of 294.185 g/mol and is orange in color. Most commonly it is acidified and utilized in portable assemblies used by police to test whether a suspect has drunk alcohol or not. It oxidizes ethyl alcohol to acetic acid and thus Potassium dichromate gives an easy identification by changing its color from orange to green.

It oxidizes as



In water Potassium dichromate dissociates as

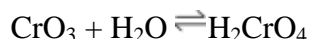


Negatively charged radicals of Chromium oxide attack the carbon atom containing a partial positive charge and bring about the chemical transition.

It reacts with Sulfuric acid as:



Chromic acid (H_2CrO_4) is formed through the reaction



Chromic acid is a very strong oxidizing agent, known for its high activity for organic oxidations.

1 Molar solution of potassium dichromate was made by dissolving 29.41 gram of Potassium dichromate in 100ml water. 10ml sulfuric acid was added to make the solution acidified. 4ml, 6ml and 10ml of this solution were added in 10ml of methanol each and a reaction time of 4hours was given. Stirring and irradiation by ultraviolet light continued for the entire reaction time. Reaction mixtures were very viscous and dark green in color so the samples were filtered to remove the solid particles. The reaction mixtures were then analyzed using high performance liquid chromatography. The reaction mixture was dark brown in color and the color disappeared on filtration.

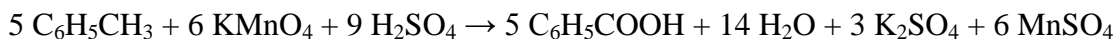


Figure 3-7: Waste material during the filtration of samples of Potassium dichromate

3.6.3 Oxidation of Methanol using acidified Potassium Permanganate as Oxidant

Potassium permanganate, KMnO_4 , is also known as Condy's crystals. It is a very active oxidant and has a molar mass of 158.034 g/mol.

Potassium permanganate has been reported to convert aldehydes and even alkyl groups to respective carboxylic acids, for example; [42]



1 Molar solution of potassium permanganate was made by dissolving 15.80 gram of Potassium permanganate in 100ml water. 10ml sulfuric acid was added to make the solution acidified. 4ml, 6ml and 10ml of this solution were added in 10ml of methanol each and a reaction time of 4hours was given. Stirring and irradiation by ultraviolet light continued for the entire reaction time. The reaction mixtures were then analyzed. The reaction mixture was of black color and was filtered before analysis but the color was retained even after filtration using Nano filters.

3.6.4 Oxidation of Methanol using Hydrogen peroxide as oxidant

Hydrogen peroxide is the most widely used oxidizing agent for organic oxidations. It is highly unstable and dissociates in to hydroxyl ions. The dissociation occurs under different conditions including thermal dissociation, dissociation under ultraviolet light and dissociation under the influence of a metal catalyst. Because we were using ultraviolet light in our experimental setup so hydrogen peroxide was expected to dissociate under our conditions and produce hydroxyl ions.

Hydrogen peroxide dissociates as:



Three reaction assemblies were setup to test the performance of Hydrogen peroxide, for the oxidation of methanol. 4ml, 6ml and 10ml of hydrogen peroxide were added in 10ml of methanol and a reaction time of 4hours was given. Stirring and irradiation by ultraviolet light continued for the entire reaction time. The reaction mixtures were then analyzed using high performance liquid chromatography.

3.6.5 Oxidation of methanol using a combination of Molybdenum Oxide catalyst and Hydrogen peroxide

Owing to the very strong support from literature regarding the use of Hydrogen Peroxide as an oxidizing agent under ultraviolet light, it was also tested for its performance in combination with a catalyst.

Molybdenum Oxide is photo catalyst, which is known for oxidation reactions in the presence of ultraviolet light. It was used in combination with hydrogen peroxide to draw a comparison between catalytic oxidation and non-catalytic oxidation of methanol.

First, 200mg of Molybdenum Oxide was added in 10ml of methanol and 10ml of Hydrogen peroxide was added, the reaction was so vigorous that the glass beaker exploded and reaction mixture splashed. To counter this problem, Hydrogen peroxide was added in steps of 1ml each, with continuous stirring.

3.7 Development of Kinetic data

Kinetic data of the reaction was needed to design the reactor. After having tested four different oxidants for the oxidation of methanol to formic acid, and combination of Molybdenum Oxide catalyst and hydrogen peroxide, it was found that the catalytic reaction gave best results so time concentration data was developed for it.

Samples were taken periodically over a time period of 3 hours and samples were spontaneously analyzed using HPLC, to get time-concentration data (Results attached in Annexure B).

Chapter

4 Results and Discussion

All the samples were analyzed using High Performance Liquid Chromatography (HPLC). Through the results of standard solutions of Formic Acid, it was analyzed that the peak of Formic Acid, the component of interest, must be somewhere between 4.8mins and 5.3mins, and the height of the peak will be somewhere between 50-350 absorbance units. The peak can slightly change the position due to the change of pH, temperature and other related factors.

4.1 Oxidation of Methanol using Citric Acid

HPLC results of all the three samples of Citric Acid showed that no considerable amount of Formic Acid was formed during the reaction. The peaks did not match any standard peaks and were only small signals caused by impurities.

Sample Name: 4ml citric acid 15-10-2015

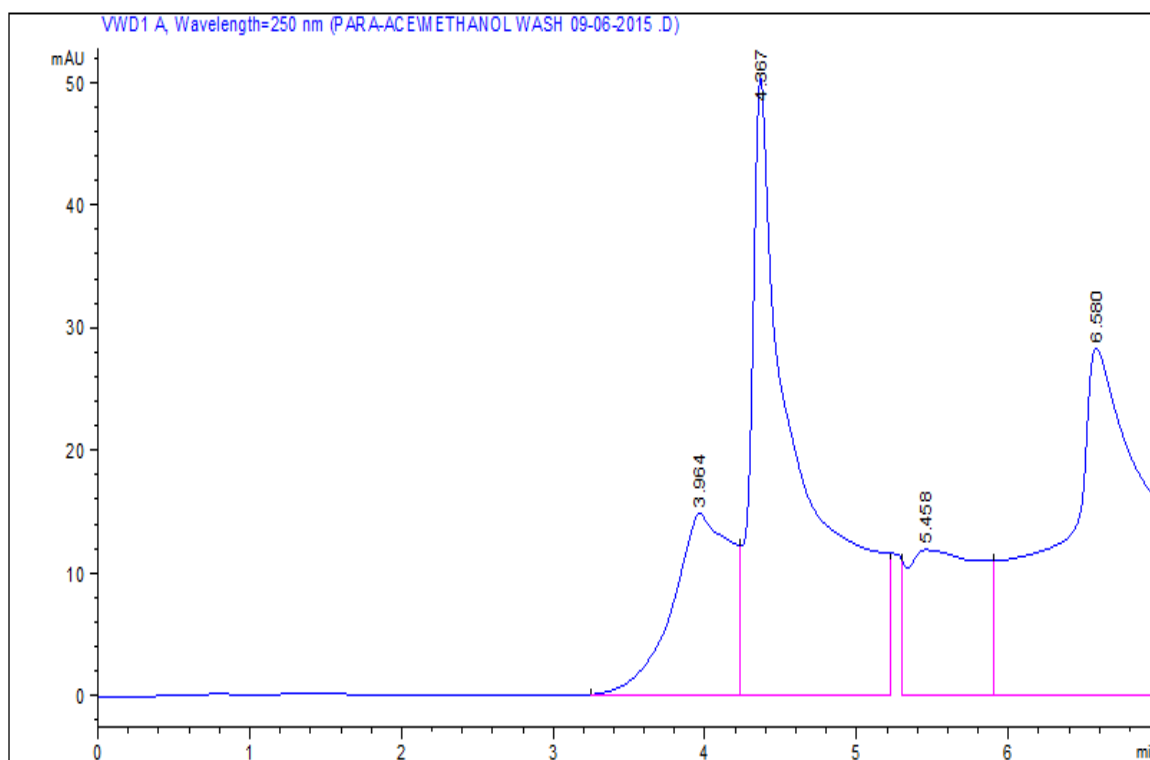


Figure 4-1: HPLC result of sample with 4ml Citric Acid

Sample Name: 6ml citric acid 15-10-2015

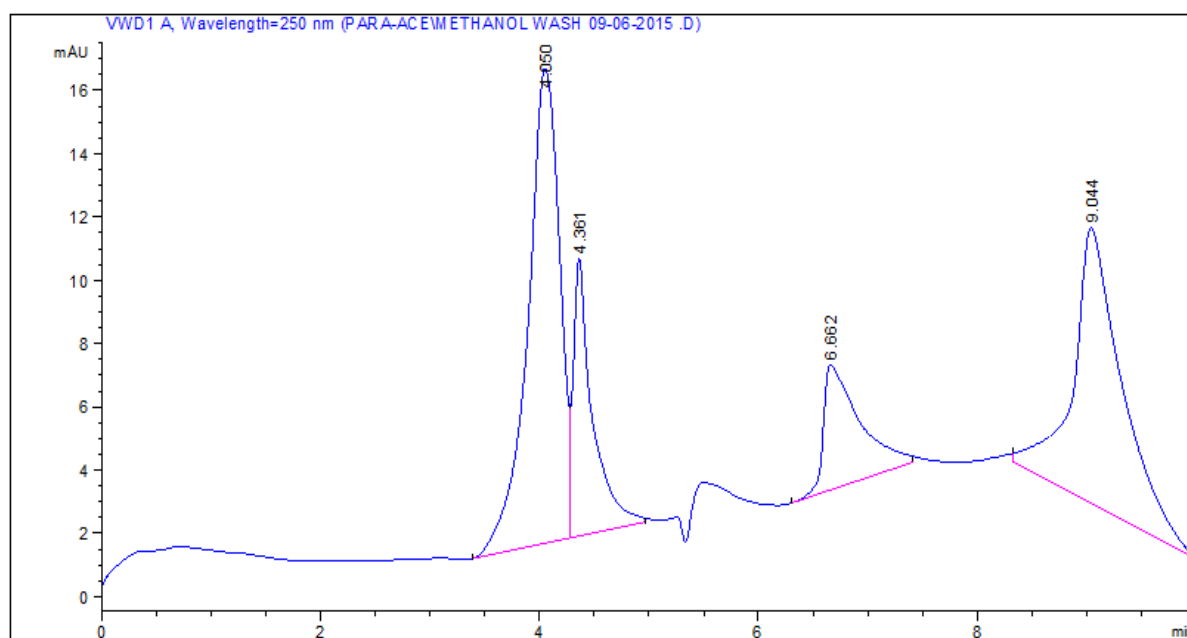


Figure 4-2: HPLC result of sample with 6ml Citric Acid

Sample Name: 10ml citric acid 15-10-2015

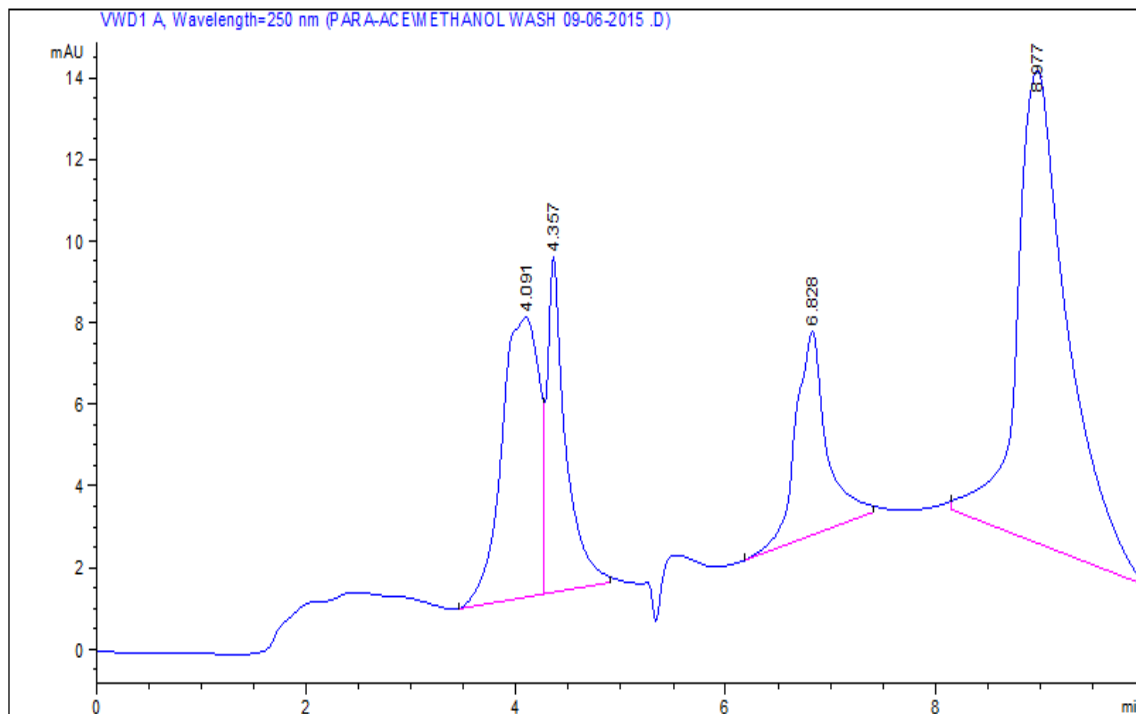


Figure 4-3: HPLC result of sample with 10ml Citric Acid

4.2 Oxidation of Methanol using Potassium dichromate

Potassium dichromate has a characteristic of oxidizing ethyl alcohol to acetic acid, and gives an easy identification by changing its color from orange to green.

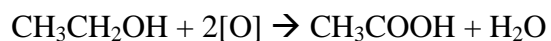


Figure 4-4: Characteristic change of color in the samples with Potassium dichromate

Color of the reaction mixture did change from dark orange to dark green color, but the HPLC results showed that very little amount of Formic Acid was formed. The second peak in the figures represents formic acid. Formic acid is a highly volatile compound and some of its amount is also expected to be evaporated due to the highly heat liberating reaction of chromic acid.

Sample Name: 4ml k2cr2o 15-10-2015

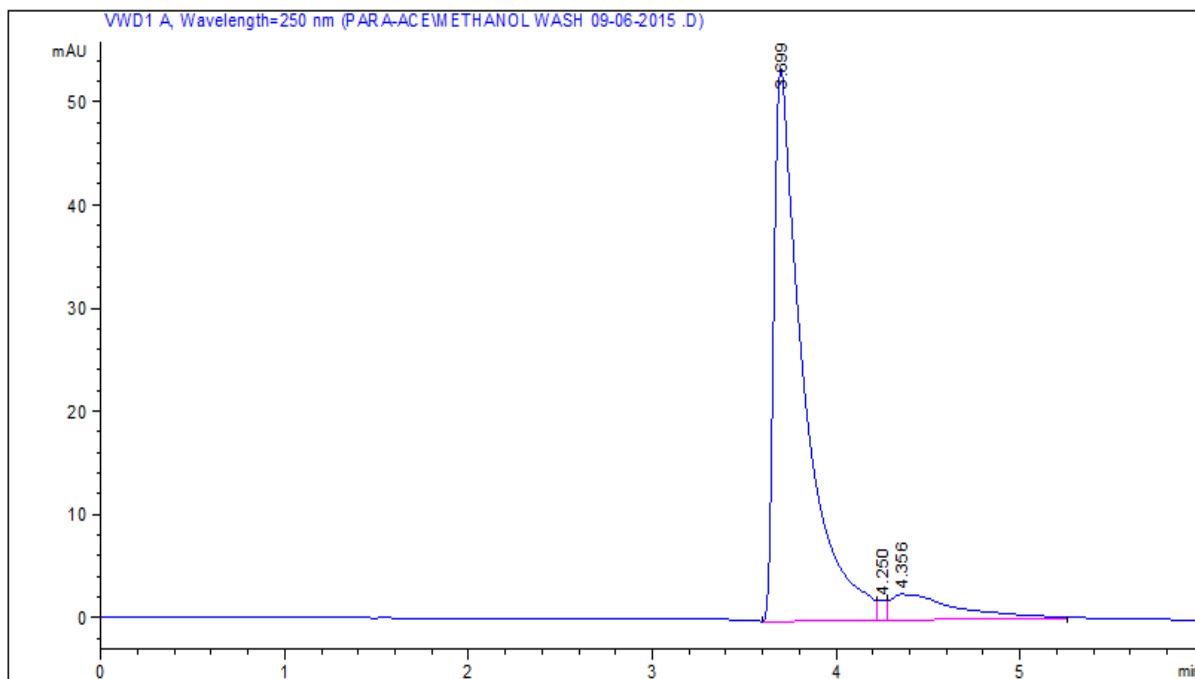


Figure 4-5: HPLC result of sample with 4ml Potassium dichromate

Sample Name: 6ml k2cr2o 15-10-2015

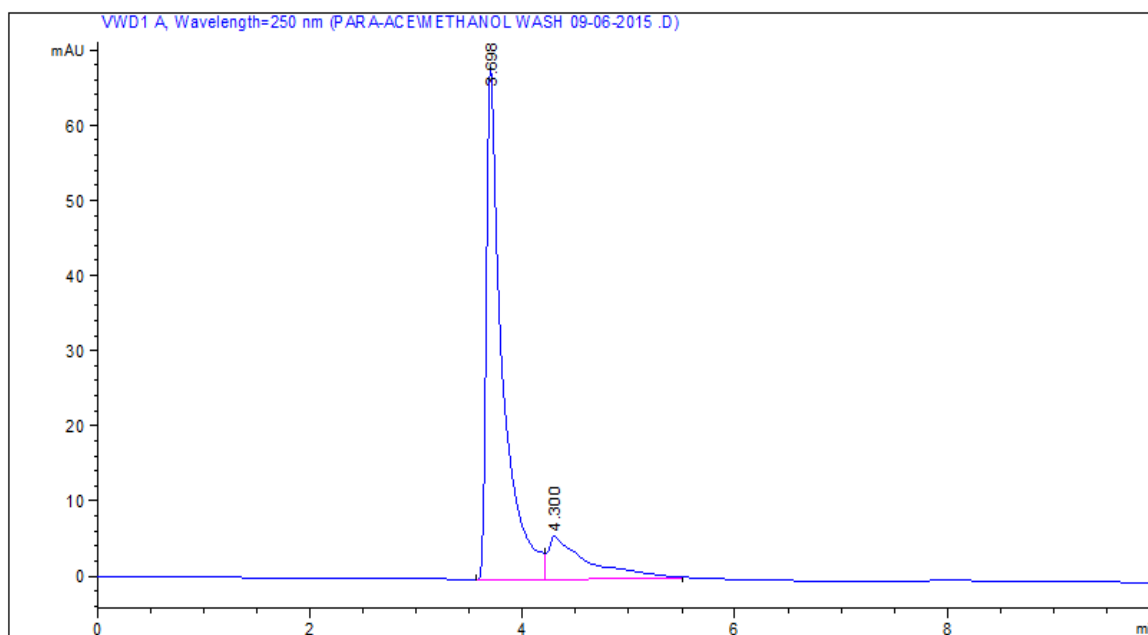


Figure 4-6: HPLC result of sample with 6ml Potassium dichromate

Sample Name:10ml k2cr2o 15-10-2015

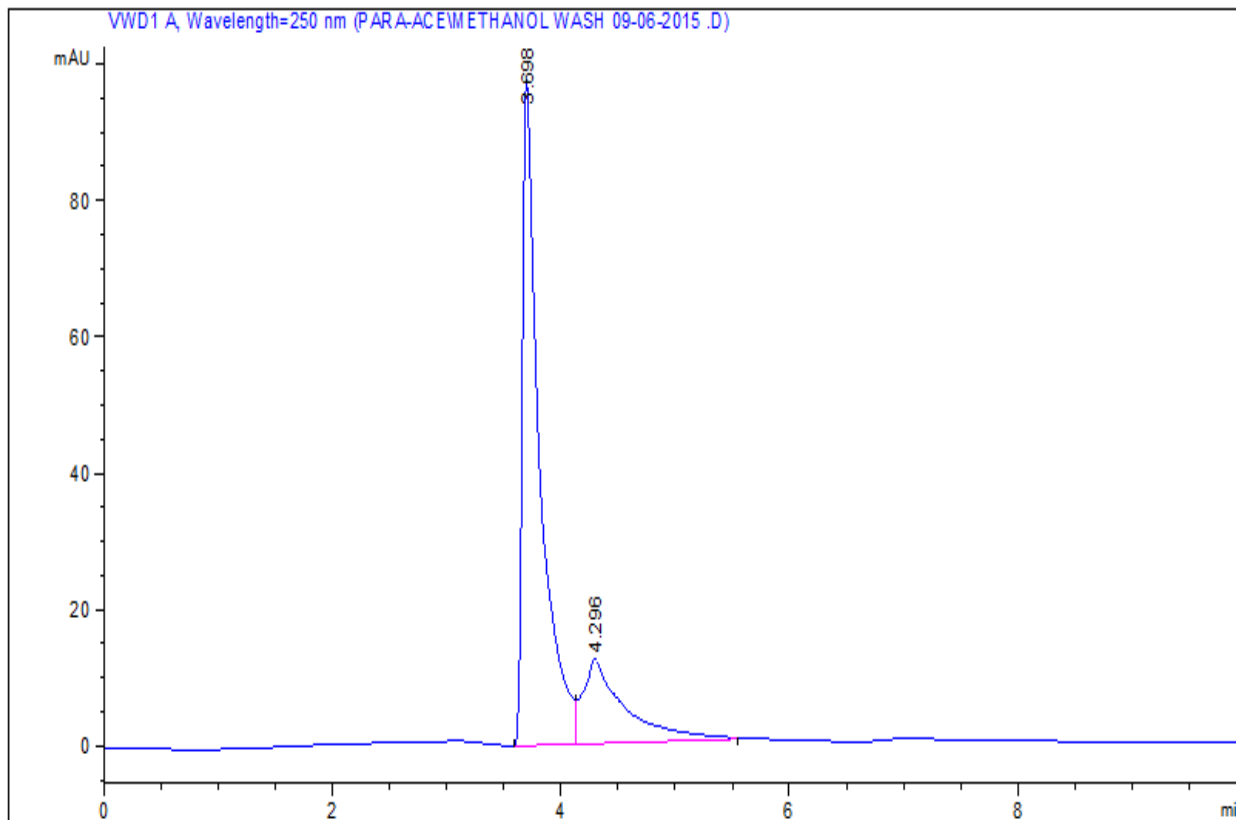


Figure 4-7: HPLC result of sample with 10ml Potassium dichromate

The first peak represents the by-product Potassium bisulfate (KHSO_4); however, peak was not verified by running standard solution of potassium bisulfate on HPLC because of its vigorous reactions which can damage the HPLC column.

4.3 Oxidation of methanol using Pottasium permanagante

HPLC results of samples oxidized from Pottasium permanaganate show a single sharp peak, but this peak does not match with the standard peaks of Formic Acid, as its position is different and it shows very huge absorption while the stadard solutions of Formic acid did not show such huge absorption even at 100% concentration. This peak matches with the peaks seen in the results of Potassium dichromate, there it was potassium bisulphate so it had low absorbance, but here it is pottasium sulphate which has a higher absorption band. Results show that Formic Acid is not present in these samles.

Sample Name: 4 ml KMnO4 15-10-2015

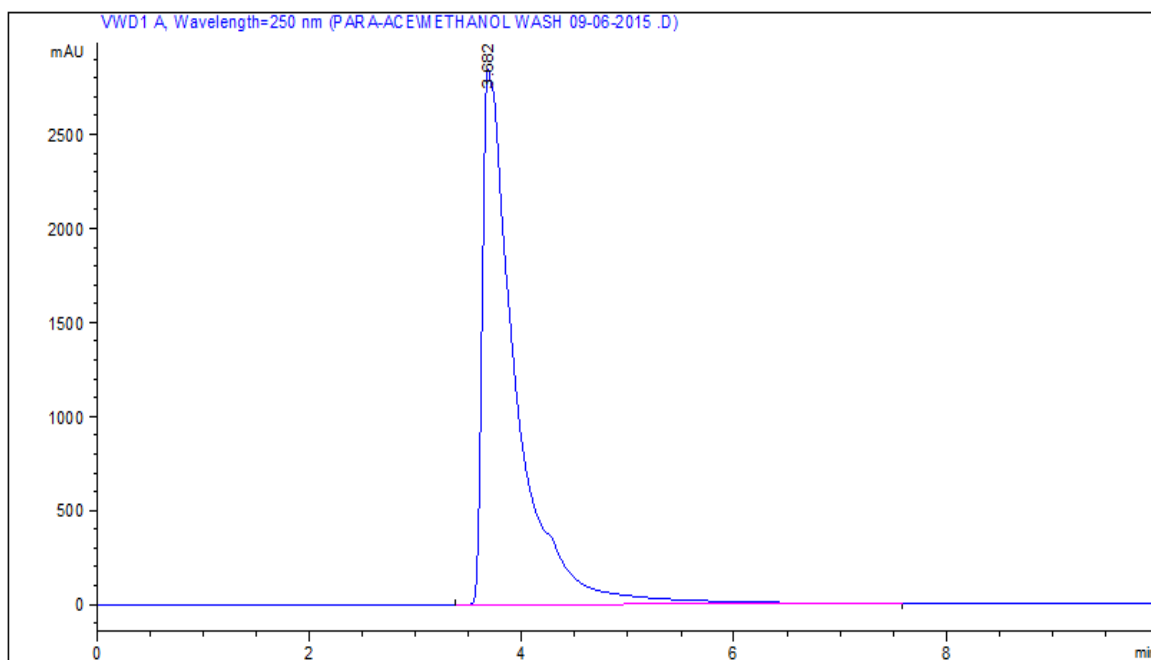


Figure 4-8: HPLC result of sample with 4ml Potassium permanganate

Sample Name: 6 ml KMnO4 15-10-2015

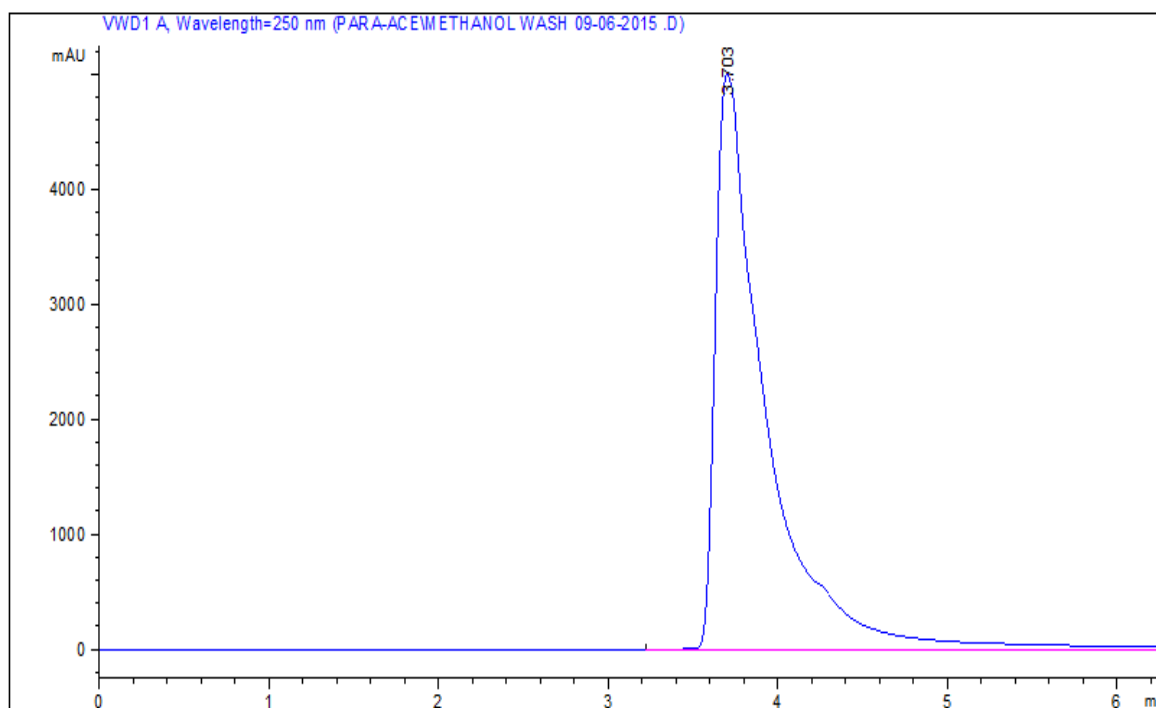


Figure 4-9: HPLC result of sample with 6ml Potassium Permanganate

Sample Name: 10 ml KMnO4 15-10-2015

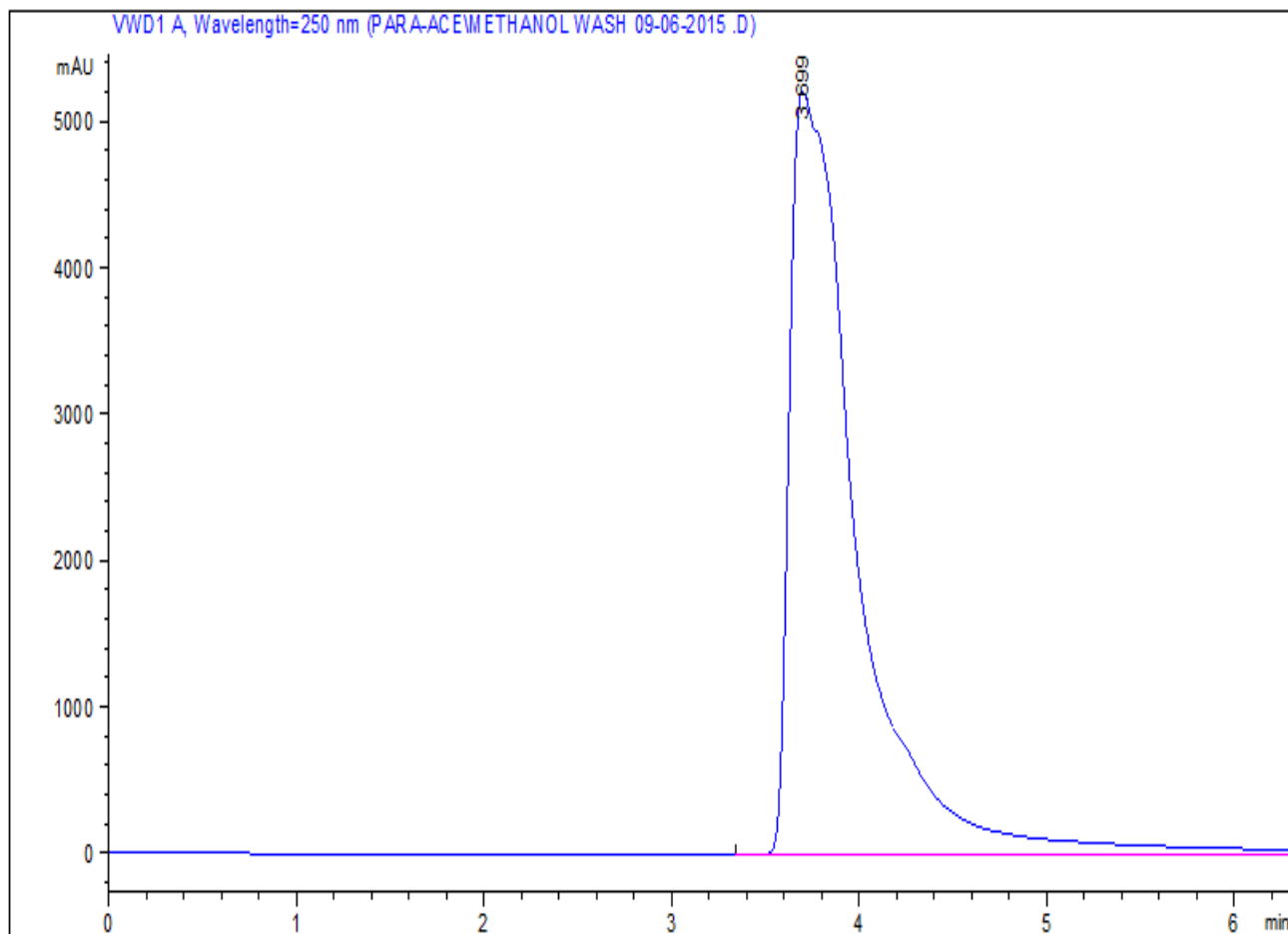


Figure 4-10: HPLC result of sample with 10ml Potassium Permanganate

4.4 Oxidation of Methanol using Hydrogen Peroxide

HPLC results of the samples oxidized using hydrogen peroxide showed a single peak, but this peak does not match with the standard peaks of Formic Acid as all three of these peaks show huge absorption while Formic acid does not show such huge absorption in the purest form. These peaks were verified to be of hydrogen peroxide, by running standard solution of 50% hydrogen peroxide, also that the area under these peaks increased with the increase in hydrogen peroxide concentration.

Sample Name: 4ml h2o2 15-10-2015

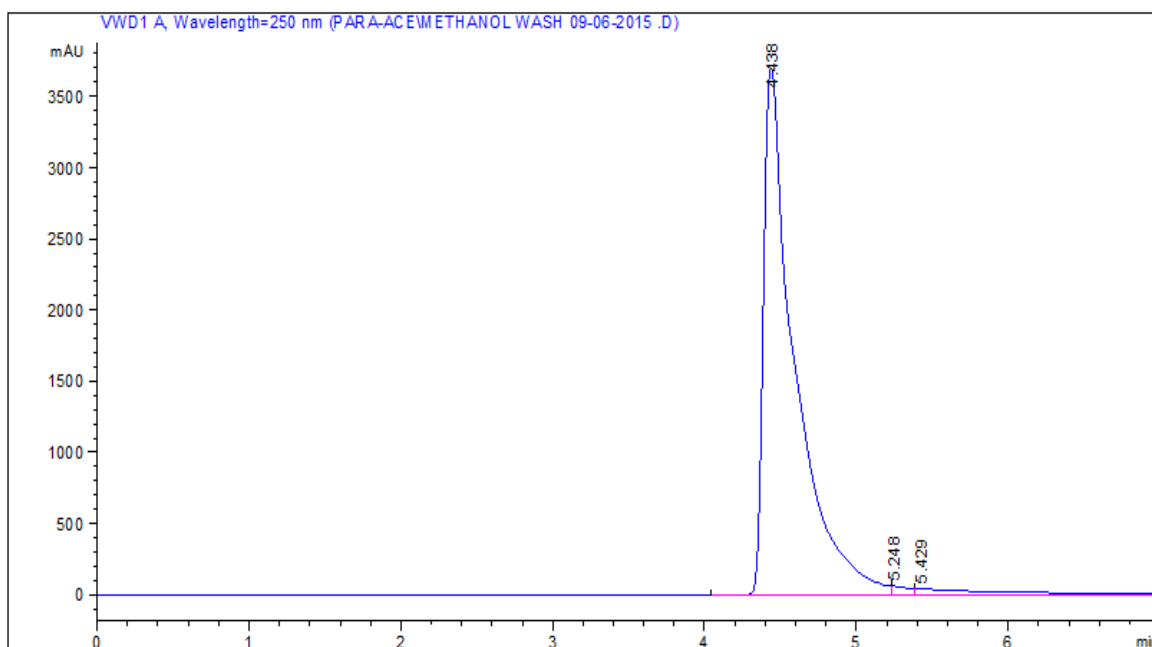


Figure 4-11: HPLC result of sample with 4ml Hydrogen peroxide

Sample Name: 6ml h2o2 15-10-2015

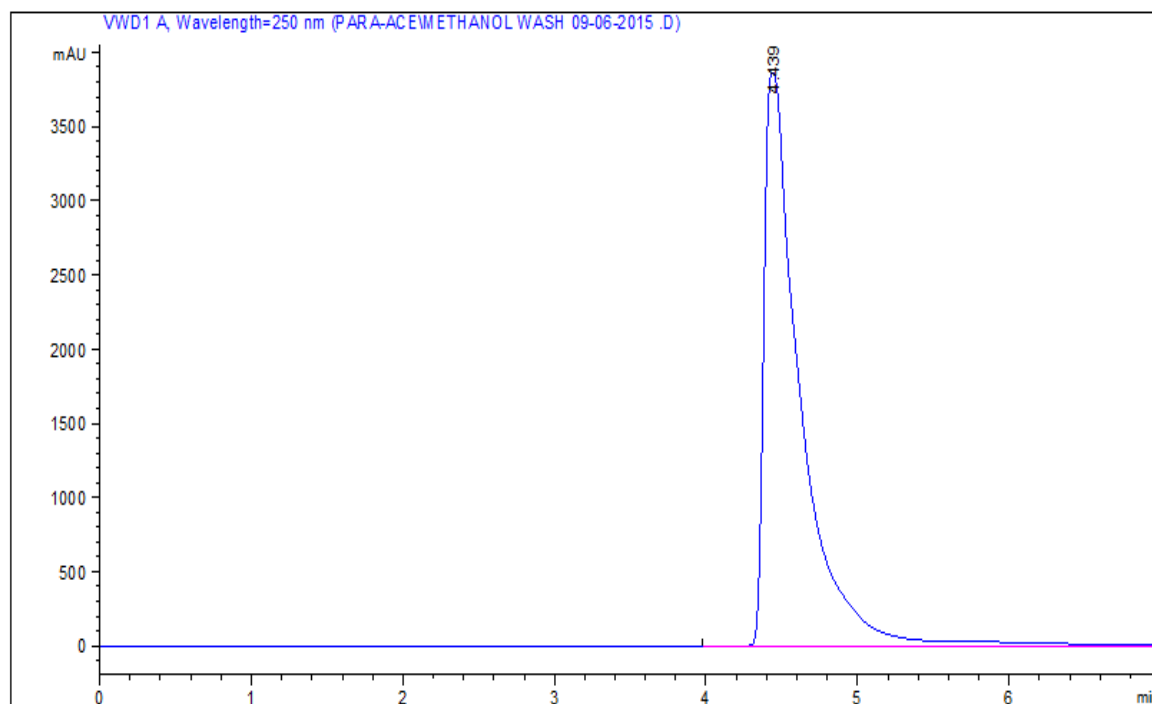


Figure 4-12: HPLC result of sample with 6ml Hydrogen peroxide

Sample Name: 10ml h2o2 15-10-2015

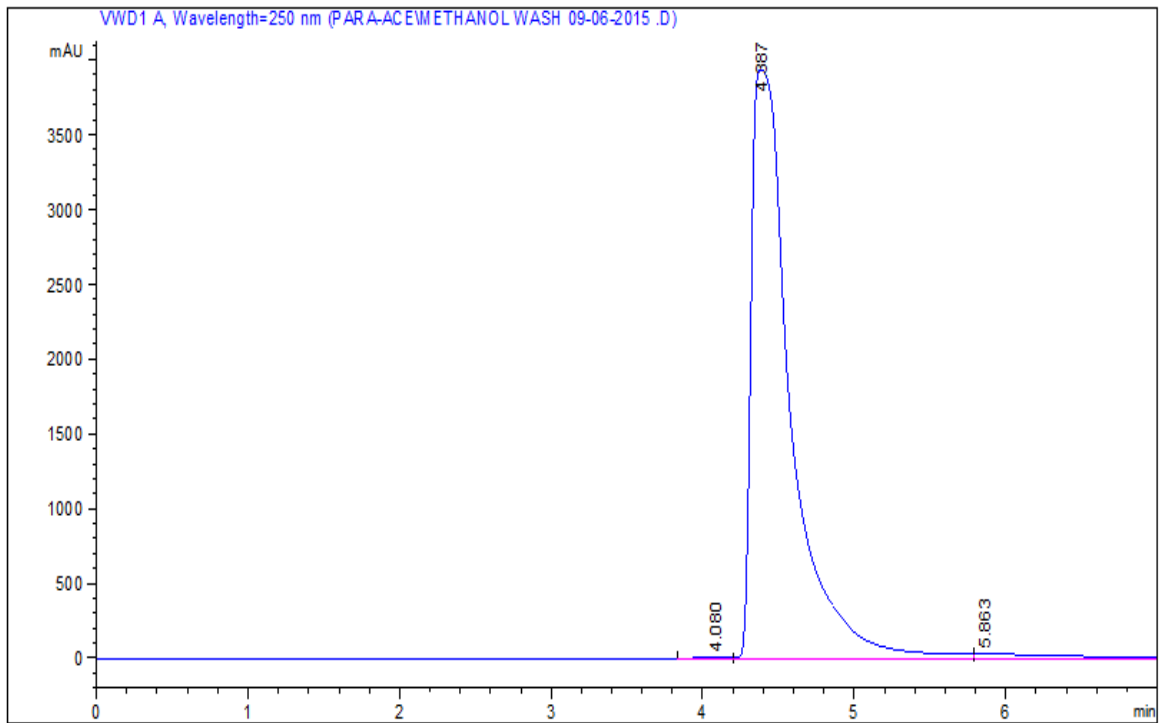


Figure 4-13: HPLC result of sample with 10ml Hydrogen peroxide

Sample Name: h2o2 16-10-2015

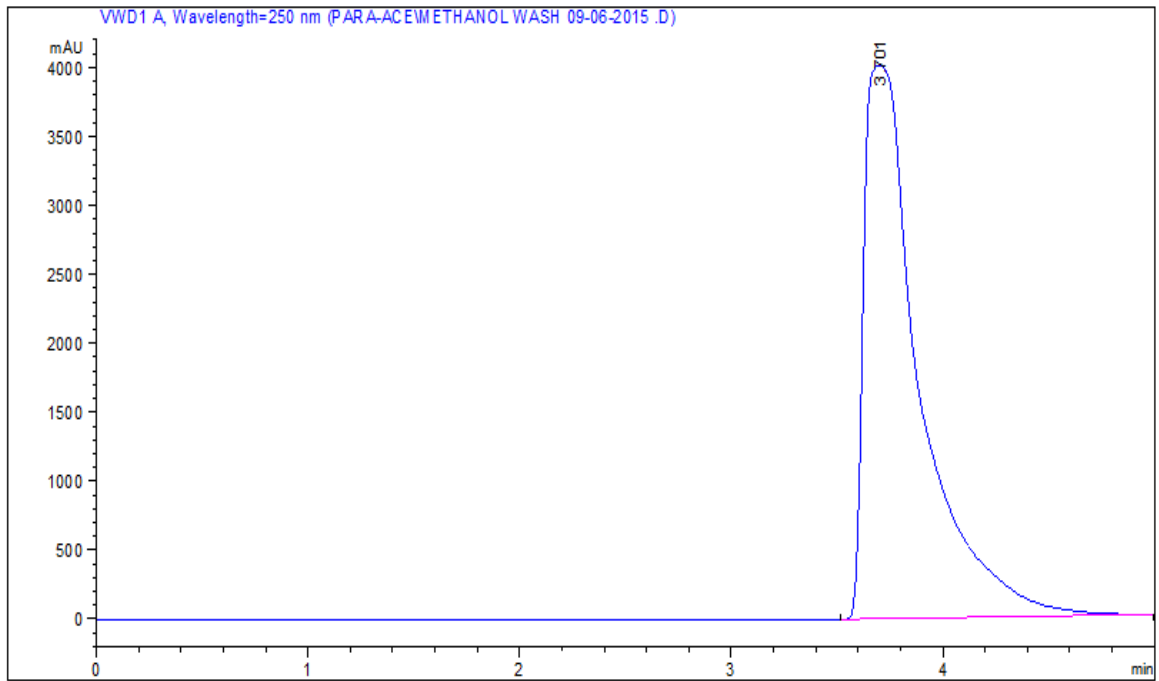


Figure 4-14: HPLC result of pure Hydrogen peroxide

Formic acid is not formed because the hydrogen peroxide, which is the oxidizer, did not dissociate. 254nm wavelength was used as a source of energy but results show that this energy is not enough. Although 254nm wavelength is generally used for organic oxidation reactions [34] but Melanie et al reported the use of ultraviolet light of 220nm wavelength for the dissociation of hydrogen peroxide [43]. Dissociation of hydrogen peroxide can be achieved either by using ultraviolet light of lower wavelength or by employing a catalyst.

4.5 Oxidation of methanol using combination of Molybdenum oxide catalyst and ultraviolet light

To improve the dissociation of Hydrogen peroxide, Molybdenum oxide catalyst was used in combination with ultraviolet light of 254nm. Results showed that hydrogen peroxide dissociated under the influence of catalyst. As the time proceeds concentration of hydrogen peroxide kept decreasing and the concentration of formic acid kept increasing until it became constant after 3 hour.

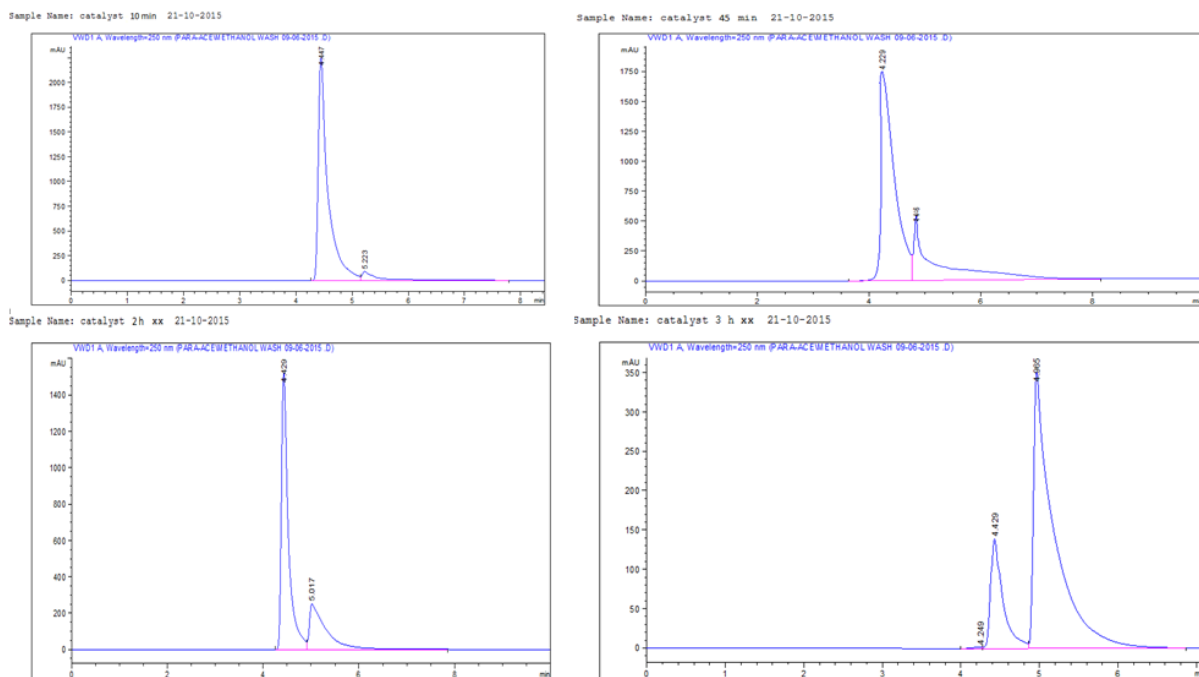


Figure 4-15: Change of concentrations with time

Change in the absorption of Formic acid was recorded, and matched with standard gradient curve, to obtain the concentration of Formic Acid. The Time-Concentration data is shown below.

Table 4-1: Time-HPLC Absorbance-Concentration data for catalytic conversion

Time (mins)	Area under absorption curve (mAU*s)	Concentration (%)
0	0	0
5	1473.41	6.1
10	1786.81	10
20	1894.53	13
45	4332.11	51
75	4997.96	63
120	6060.55	77
150	6356.83	81
180	6560.87	82

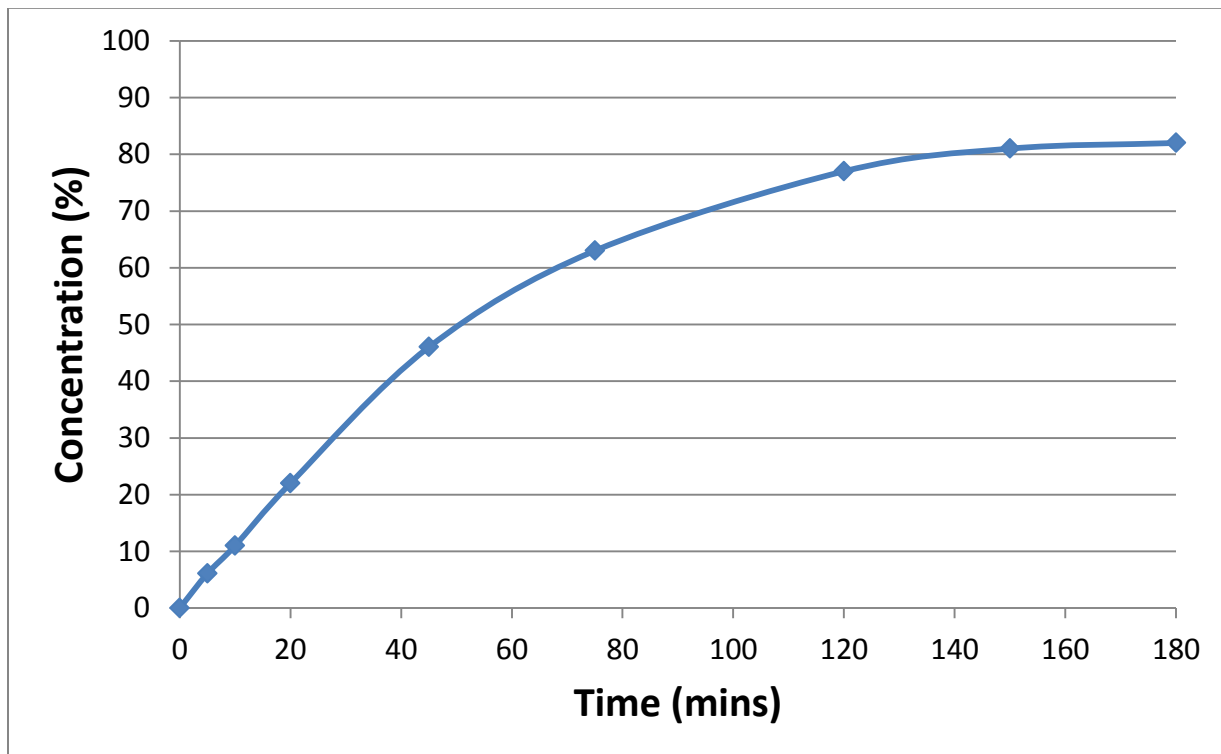


Figure 4-16: Time Vs. Conversion for catalytic reaction

Chapter

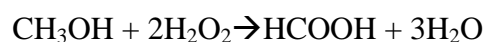
5 Reactor Design

5.1 Efficient oxidizing scheme

From the results of all the tested oxidizing agents, it was concluded that Hydrogen peroxide when used with the Molybdenum oxide catalyst, gives the most efficient conversion of Methanol to Formic Acid. Up to 82% conversion was achieved. Based on these results, reaction kinetics was to be established for this reaction. Reaction kinetics values are then needed to design a reactor for this particular reaction.

5.2 Reaction kinetics

When methanol reacts with Hydrogen peroxide, the overall reaction is:



Samples were analyzed on HPLC to find the formation of Formic Acid. Stoichiometric ratios i.e. 10ml of methanol and 11.6ml of hydrogen peroxide were reacted and respectively their molarity was 0.2475mol/ml methanol and 0.4950mol/ml hydrogen peroxide.

Based on the stoichiometry of the reaction, number of moles and concentrations were calculated for all the components;

Table 5-1: Number of moles of each component during reaction

Time (mins)	Methanol (moles)	H ₂ O ₂ (moles)	Formic (moles)	Water (moles)
0	0.2475	0.4950	0.0000	0.0000
5	0.2228	0.4455	0.0248	0.0743
10	0.1982	0.3965	0.0493	0.1478
20	0.1546	0.3093	0.0929	0.2786
45	0.0773	0.1546	0.1702	0.5106
75	0.0286	0.0572	0.2189	0.6567
120	0.0066	0.0132	0.2409	0.7228
150	0.0013	0.0025	0.2462	0.7387
180	0.0002	0.0005	0.2473	0.7418

Based on the number of moles and the volume, Concentrations of each component were calculated.

Table 5-2: Molar concentration of each component during reaction

Time (mins)	Methanol Con (mol/ml)	H ₂ O ₂ Con (Mol/ml)	Formic Acid con (mol/ml)	Water con (mol/ml)	Methanol Rate
0	0.011458	0.022917	0.000000	0.000000	0.000000
5	0.010313	0.020625	0.001146	0.003438	0.003819
10	0.009178	0.018356	0.002280	0.006841	0.003800
20	0.007159	0.014318	0.004299	0.012898	0.003583
45	0.003579	0.007159	0.007879	0.023637	0.002918
75	0.001324	0.002649	0.010134	0.030402	0.002252
120	0.000305	0.000609	0.011154	0.033461	0.001549
150	0.000058	0.000116	0.011400	0.034201	0.001267
180	0.000010	0.000021	0.011448	0.034344	0.001060

The general definition of the rate of reaction is defined as; change in number of moles of a component in unit volume in unit time. Rate of conversion of methanol was calculated based on the general formula:

$$r = \frac{\text{(Change in number of moles of i)}}{\text{(Time * Volume of reaction medium)}}$$

It cannot be predicted from stoichiometry that on what factors the rate of reaction depends on and whether a reaction is elementary reaction or non-elementary reaction. Elementary reactions are those in which the exponents of the rate equation are equal to the stoichiometric coefficients, while in non-elementary reactions the exponents of the rate equation are not equal to the stoichiometric coefficients. To avoid any use of assumption, the general formula was considered to find the order and kinetic factor:

$$r = k C_A^\alpha C_B^\beta$$

Natural logarithm was taken on both sides and the formula became

$$\ln(r) = \ln k + \alpha \ln(C_A) + \beta \ln(C_B)$$

C_A and C_B are the concentrations of methanol and Hydrogen peroxide respectively.

A matrix was established by using the experimental values for the above formula at three different times (i.e. 45mins, 120mins and 180mins).

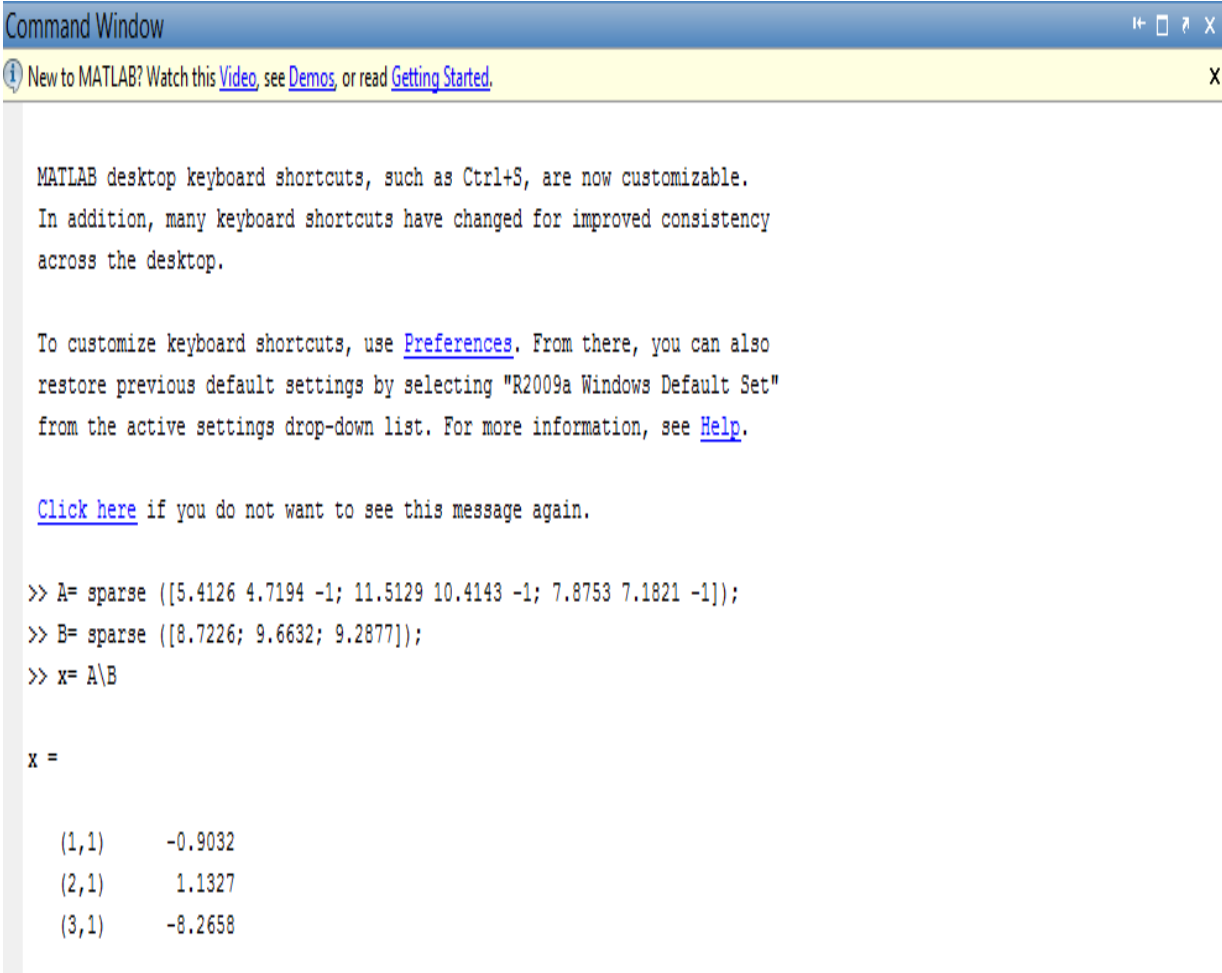
$$\ln(r_{45}) = \ln k + \alpha \ln(C_{A45}) + \beta \ln(C_{B45})$$

$$\ln(r_{120}) = \ln k + \alpha \ln(C_{A120}) + \beta \ln(C_{B120})$$

$$\ln(r_{180}) = \ln k + \alpha \ln(C_{A180}) + \beta \ln(C_{B180})$$

$$\begin{pmatrix} 05.4126 & 04.7194 & -1 \\ 11.5129 & 10.4143 & -1 \\ 07.8753 & 07.1821 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \\ \ln k \end{pmatrix} = \begin{pmatrix} 8.7226 \\ 9.6632 \\ 9.2877 \end{pmatrix}$$

Matrix was solved on MATLAB to find the values of α , β and $\ln k$.



The screenshot shows the MATLAB Command Window with the following content:

```

Command Window
New to MATLAB? Watch this Video, see Demos, or read Getting Started.

MATLAB desktop keyboard shortcuts, such as Ctrl+S, are now customizable.
In addition, many keyboard shortcuts have changed for improved consistency
across the desktop.

To customize keyboard shortcuts, use Preferences. From there, you can also
restore previous default settings by selecting "R2009a Windows Default Set"
from the active settings drop-down list. For more information, see Help.

Click here if you do not want to see this message again.

>> A= sparse ([5.4126 4.7194 -1; 11.5129 10.4143 -1; 7.8753 7.1821 -1]);
>> B= sparse ([8.7226; 9.6632; 9.2877]);
>> x= A\B

x =

(1,1)    -0.9032
(2,1)     1.1327
(3,1)    -8.2658
  
```

Figure 5-1: Solution of matrix on MATLAB

Final values were

Table 5-3: Rate equation values for catalytic conversion

kinetic factor k	0.000220
α	-0.903200
β	1.132700
Order of reaction ($\alpha + \beta$)	0.220000

5.3 Designing in ASPEN Plus

5.3.1 ASPEN Plus

Aspen Plus was opted because of its provision to simulate Batch Reactors. Moreover, ASPEN Plus has modules for a wide range of chemical processes and has a considerable flexibility of operations as well.

5.3.2 Specifying the components

Components of the reaction are to be specified to carry out any simulation. Specifying a component means specifying all its properties, which will then be used to calculate all the parameters of the simulation. Properties can be specified automatically by using ASPEN Plus database or could be specified manually for components which are not available in the database. The components were specified using Aspen plus data library.

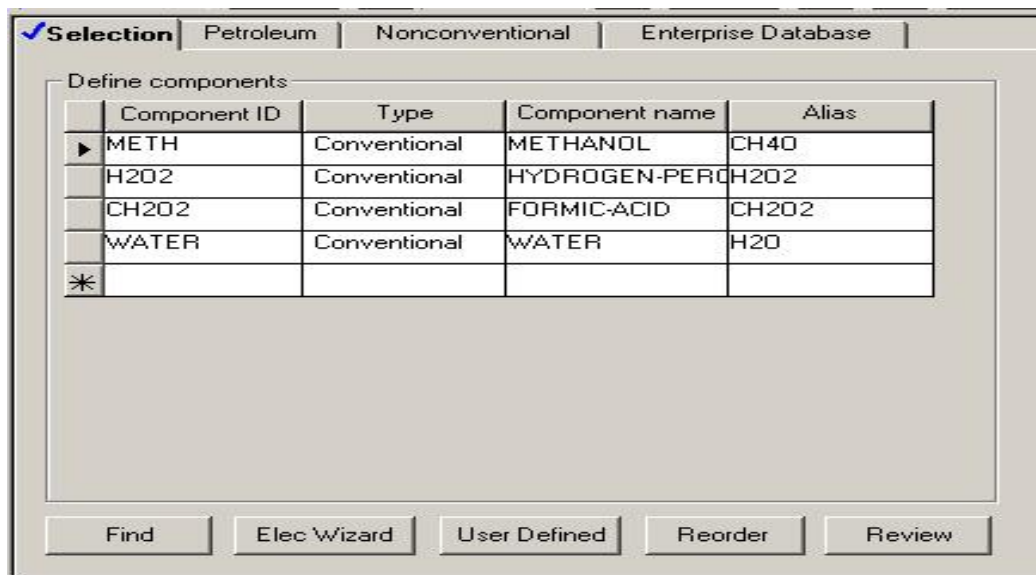


Figure 5-2: Component selection in ASPEN PLUS

5.3.3 Fluid Package

Fluid Package is the set of equation which are used by the software for calculations of a particular simulation. Selection of fluid package is very critical because the accuracy of calculations will depend on it. As all the equations are valid within certain parameters, so selection of fluid package is also dependent on the components involved in the reaction and the reaction conditions. SYSOP0 property package was chosen.

5.3.3.1 SYSOP0 Fluid Package

SYSOP0 Fluid Package is recommended for the alcohols and organic chemical reactions, in liquid phase. It considers the components to behave ideally according to Raoult's Law. According to Raoult's Law the vapor pressure of liquid depends on the fraction of its components and their binary interaction does not affect these properties. If some other fluid package is selected which is based on some other theory then the calculated values of the streams will be different, but ideal behavior was considered in this case.

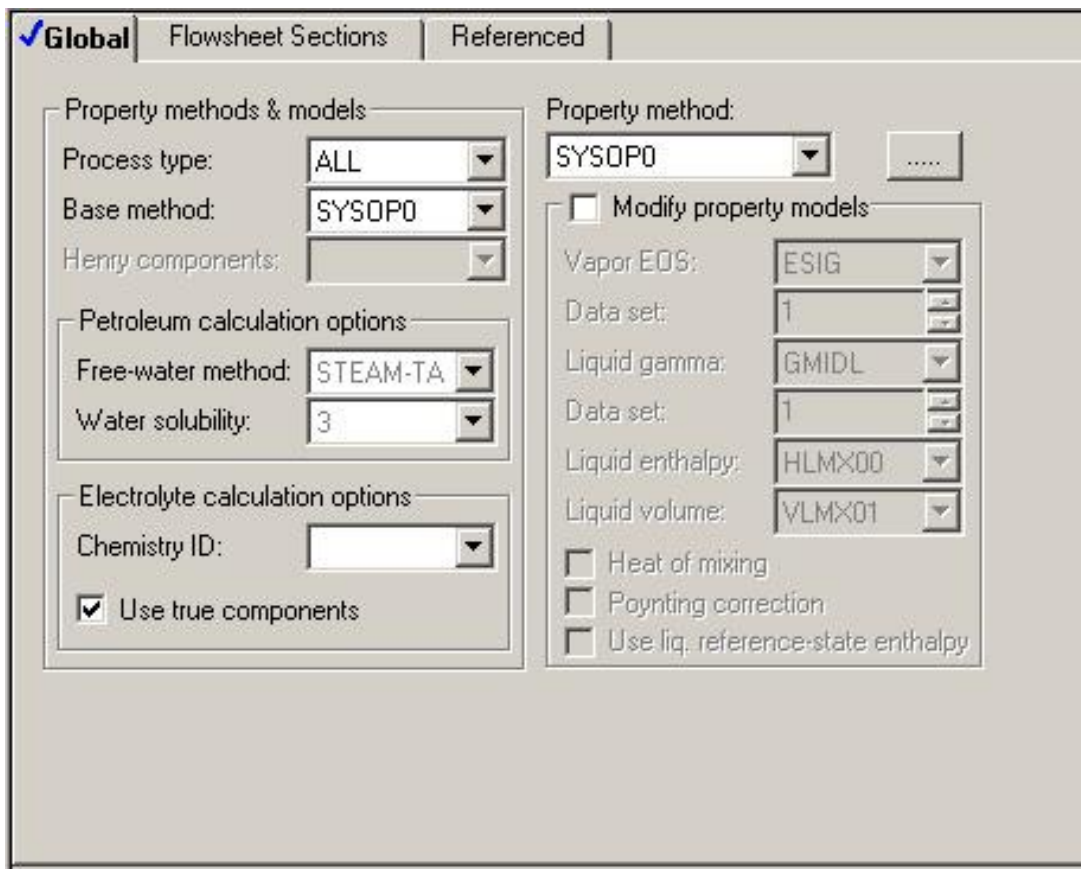
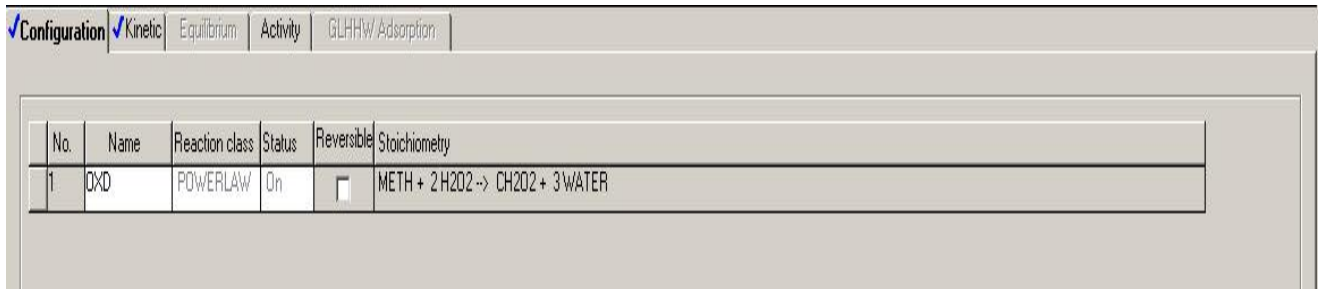


Figure 5-3: Fluid Package selection in ASPEN PLUS

5.3.4 Reaction set

Reaction set is to be defined, which includes the components of the reaction, their stoichiometric coefficients and the nature of the reaction.

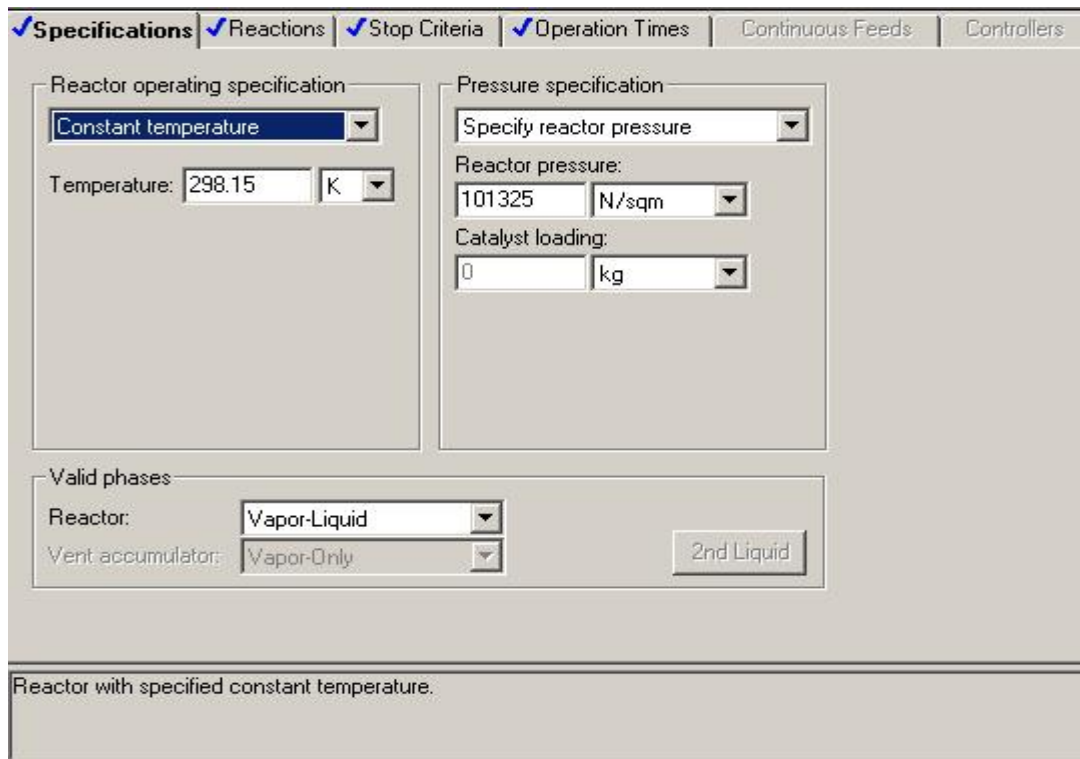


No.	Name	Reaction class	Status	Reversible	Stoichiometry
1	OXD	POWERLAW	On	<input type="checkbox"/>	METH + 2 H2O2 -> CH2O2 + 3 WATER

Figure 5-4: Defining reaction in ASPEN PLUS

5.3.5 Reaction conditions

Calculations are based on the reaction conditions, so all the conditions are to be specified. No considerable change of temperature was observed during the reaction, the temperature stayed constant around room temperature which was recorded to be 27°C, and hence the reaction was considered a constant temperature reaction. Reaction was carried out at atmospheric temperature. So the reaction was defined as room temperature, atmospheric pressure reaction.



Specifications Reactions Stop Criteria Operation Times Continuous Feeds Controllers

Reactor operating specification: Constant temperature
Temperature: 298.15 K

Pressure specification: Specify reactor pressure
Reactor pressure: 101325 N/sqm
Catalyst loading: 0 kg

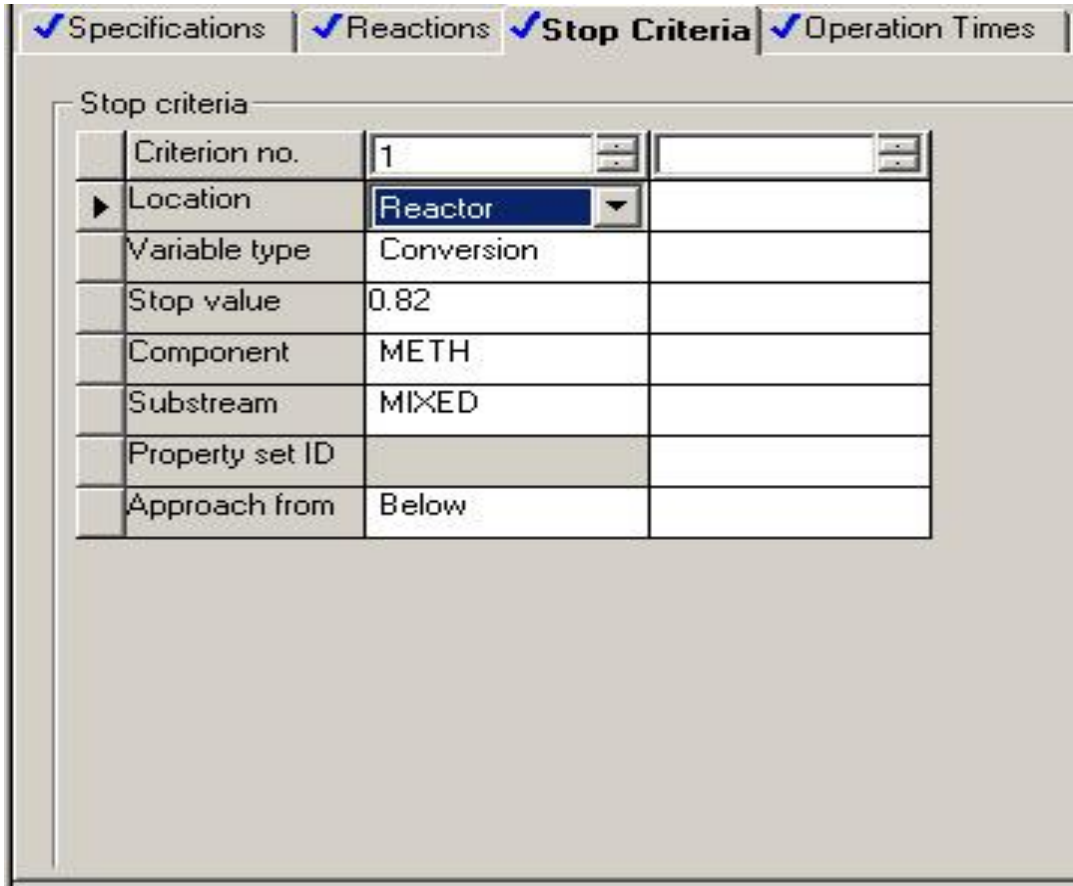
Valid phases: Reactor: Vapor-Liquid, Vent accumulator: Vapor-Only, 2nd Liquid

Reactor with specified constant temperature.

Figure 5-5: Operating conditions of reactor

5.3.6 Stop criteria

In a batch reactor, stop criteria is to be defined. Stop criteria is a parameter which if met, then the reaction stops. According to experimental data up to 82% conversion of methanol was achieved, hence 82% conversion was defined as a stop criteria.



Stop criteria			
Criterion no.	1		
Location	Reactor		
Variable type	Conversion		
Stop value	0.82		
Component	METH		
Substream	MIXED		
Property set ID			
Approach from	Below		

Figure 5-6: Stop Criteria for reaction

5.3.7 Batch reaction time

Batch reaction time is the time over which the batch will be run. If the pre-defined stop criteria is met before the batch reaction time ends, then the reaction would terminate instantly, however, if the stop criteria is not met within the batch reaction time then with the completion of batch reaction time the reaction would terminate anyway and the extent to which the stop criteria is met would be shown in the results.

In the experimental setup, the reaction concentrations were analyzed over a reaction time of 3 hours, after which concentrations became constant; hence the batch reaction time was specified to be 3 hours.

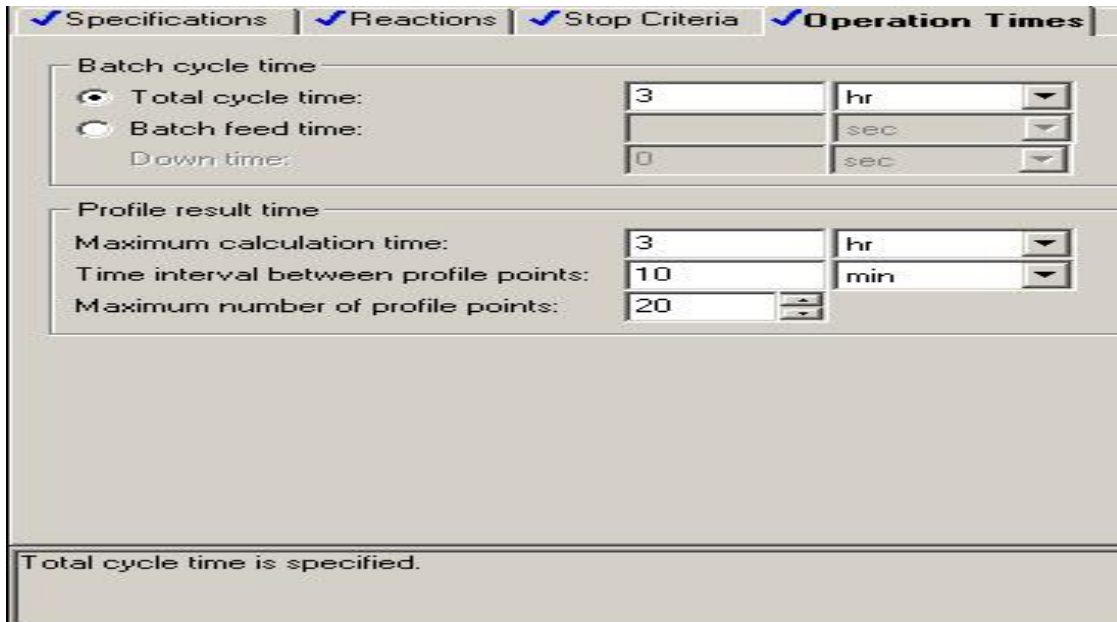


Figure 5-7: Batch reaction time

5.3.8 Simulation convergence

A simulation is said to be converged when it does not give any error and all the parameters are found compatible with each other. The discussed simulation converged, under these conditions, and no warning or error was shown.

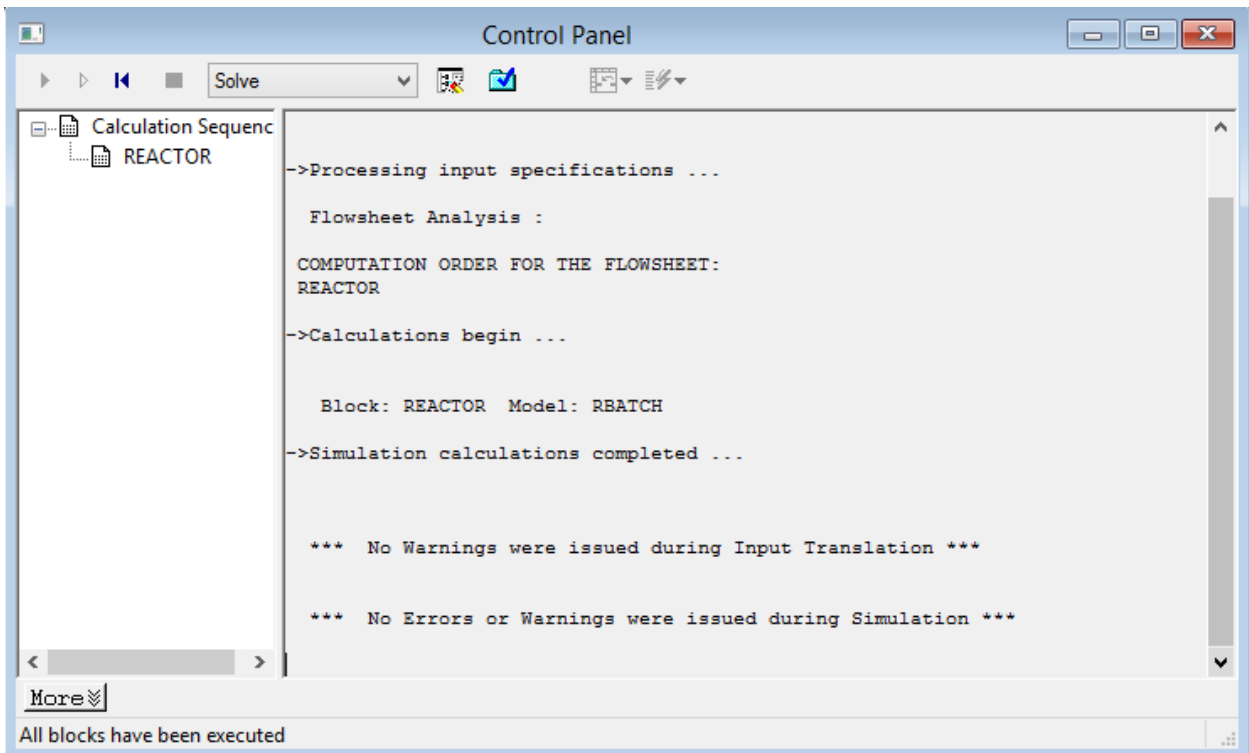


Figure 5-8: Simulation status of reactor model

5.3.9 Flow streams of the reactor

Heat and Material Balance Table			
Stream ID		FEED	PRODUCT
From			REACTOR
To		REACTOR	
Phase		LIQUID	LIQUID
Substream: MIXED			
Mole Flow	lbmol/hr		
METH		.0239299	4.30724E-3
H2O2		.0478974	8.65199E-3
CH2O2		0.0	.0196227
WATER		0.0	.0588681
Mole Frac			
METH		.3331593	.0470992
H2O2		.6668407	.0946087
CH2O2		0.0	.2145730
WATER		0.0	.6437189
Mass Flow	lb/hr		
METH		.7667678	.1380132
H2O2		1.629216	.2942945
CH2O2		0.0	.9031494
WATER		0.0	1.060527
Mass Frac			
METH		.3200221	.0576018
H2O2		.6799779	.1228283
CH2O2		0.0	.3769430
WATER		0.0	.4426269
Total Flow	lbmol/hr	.0718274	.0914501
Total Flow	lb/hr	2.395984	2.395984
Total Flow	cuft/hr	.0341157	.0393354
Temperature	F	77.00000	77.38467
Pressure	psia	14.69595	14.69595
Vapor Frac		0.0	0.0
Liquid Frac		1.000000	1.000000
Solid Frac		0.0	0.0
Enthalpy	Btu/lbmol	-88103.40	-1.2830E+5
Enthalpy	Btu/lb	-2641.186	-4897.100
Enthalpy	Btu/hr	-6328.238	-11733.37
Entropy	Btu/lbmol-R	-54.15175	-37.85167
Entropy	Btu/lb-R	-1.623375	-1.444726
Density	lbmol/cuft	2.105406	2.324878
Density	lb/cuft	70.23111	60.91157
Average MW		33.35752	26.19989
Liq Vol 60F	cuft/hr	.0335500	.0349903

Figure 5-9: Flow Streams of inlet and outlet of reactor model

5.3.10 Concentration profiles within the reactor

Figure shows a comparative plot of change of concentration within the reactor.

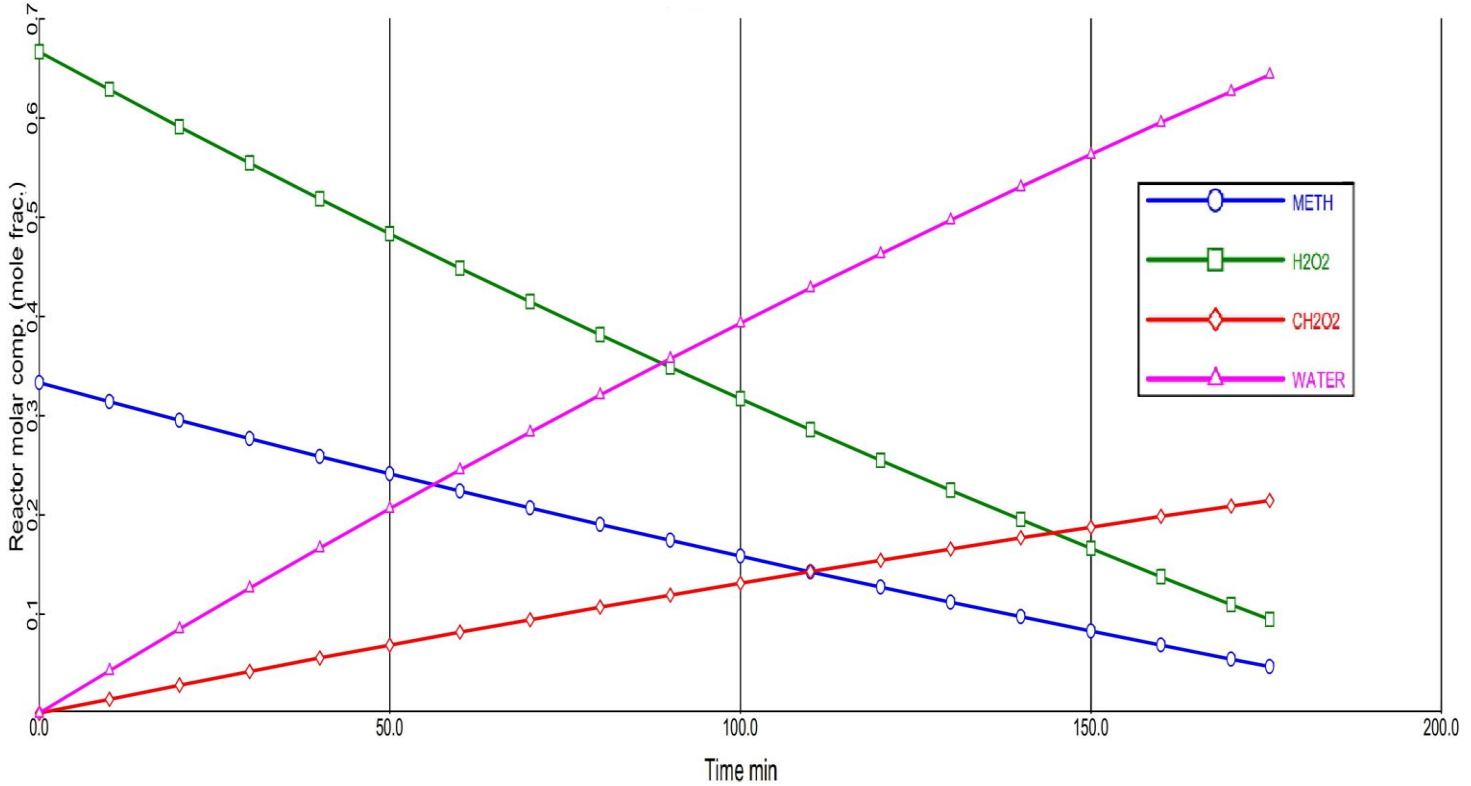


Figure 5-10: Concentration profiles within the reactor

5.4 Verification of the reaction kinetics

The two parameters for the termination of reaction, i.e. stop criteria and batch reaction time, would complement each other. In the simulation, both parameters were met at almost the same time. Stop criteria was met at 175 minutes while the experimentally determined batch reaction time was 3 hours (180 minutes), this gave the verification that reaction kinetics were rightly determined and were found to be valid over the whole reaction time.

5.5 Reactor dimensions

Dimensions of the batch reactor were calculated based on the 100kmol Methanol basis. 200kmol of Hydrogen peroxide were needed to oxidize methanol. Reaction is a constant low temperature reaction but because of the volatile nature of the components, 25% area was given to accommodate vapors. Total required volume was calculated to be 11m³.

Table 5-4: Volume of required reactor

Basis: 100 kmol Methanol		
	Methanol	Hydrogen peroxide
Moles	100 kmol	200 kmol
Molar mass	32.04 kg/kmol	34.0147 kg/kmol
Mass	3204 kg	6802.94 kg
Density	791.41 kg/m ³	1450 kg/m ³
Volume	4.0484 m ³	4.69 m ³
Total volume of reactants	8.73 m ³	
Total volume with 25% space for vapors	11 m³	

Cylindrical shaped reactor was chosen to attain better stirring and ease of cleaning. Radius was chosen to be 1 m while the height was calculated using the formula for the volume of cylinder

$$V = 2\pi r^2h$$

Table 5-5: Dimensions of cylindrical reactor

For a cylindrical shaped reactor		
Total Volume required	11 m ³	
Radius	1 m	3.00 ft
Height of reactor	1.75 m	5.74 ft

Chapter

6 Conclusions and recommendations

6.1 Conclusions:

A comparative study of Citric acid, Potassium dichromate, Potassium permanganate and Hydrogen peroxide was carried out, to test their performance, for the synthesis of Formic acid by oxidation of methanol. Ultraviolet light was used as a source of energy to achieve conversion at low temperature.

Citric Acid and acidified potassium permanganate did not synthesize any Formic Acid. Acidified potassium dichromate, however, showed a very minor production of Formic acid, other than the low yield, the reaction mixture was a very viscous dark green colored material which was filtered and material was also wasted with the filtered matter.

Hydrogen peroxide, when used solely with ultraviolet light, did not show any production of Formic Acid, however it was also observed that solely under the action of ultraviolet light, of 254nm wavelength, hydrogen peroxide is not getting dissociated.

Molybdenum Oxide catalyst was used in combination with ultraviolet light, to dissociate hydrogen peroxide. The results showed that hydrogen peroxide was getting dissociated under these conditions. Formic Acid was synthesized in a considerable amount.

Using the kinetic data of catalytic reaction, reactor was designed for the synthesis of Formic Acid.

6.2 Recommendations:

Based on our results, it is recommended that ultraviolet light of wavelength less than 220nm could be tested to achieve dissociation of hydrogen peroxide, without catalyst. Ultraviolet light of wavelength 160nm could also be tested because it is reported in literature that at 160nm wavelength carbon atom of the methanol also gets excited and is most likely to form a transition complex.

Pressurized reactors could be tested to achieve higher efficiency because the constituents of the reaction mixture are volatile and under pressure better contact could be achieved.

Nano catalyst could be coated on the stirrer; this could help in the recovery of catalyst and avoid the step of catalyst separation.

7 References

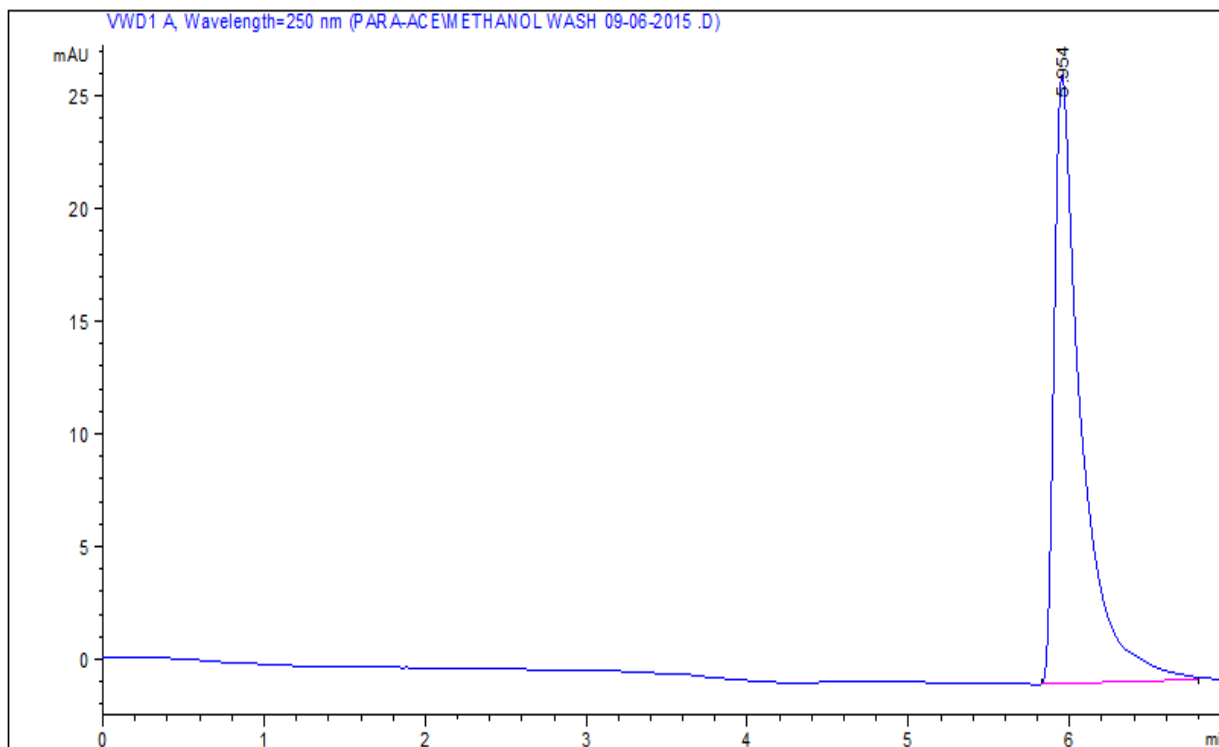
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Annexure A

Sample Name: 1.25% 06-10-2015



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.954	BB	0.1664	318.02267	27.03776	100.0000

Totals : 318.02267 27.03776

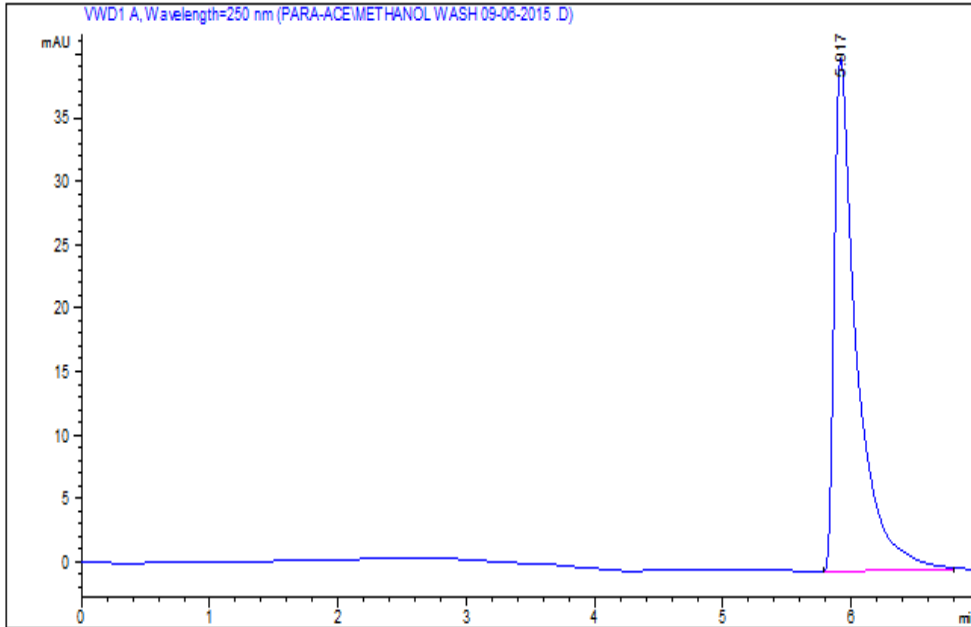
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

=====
Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 2.5% 08-10-2015



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.917	BB	0.1743	492.70102	40.41624	100.0000

Totals : 492.70102 40.41624

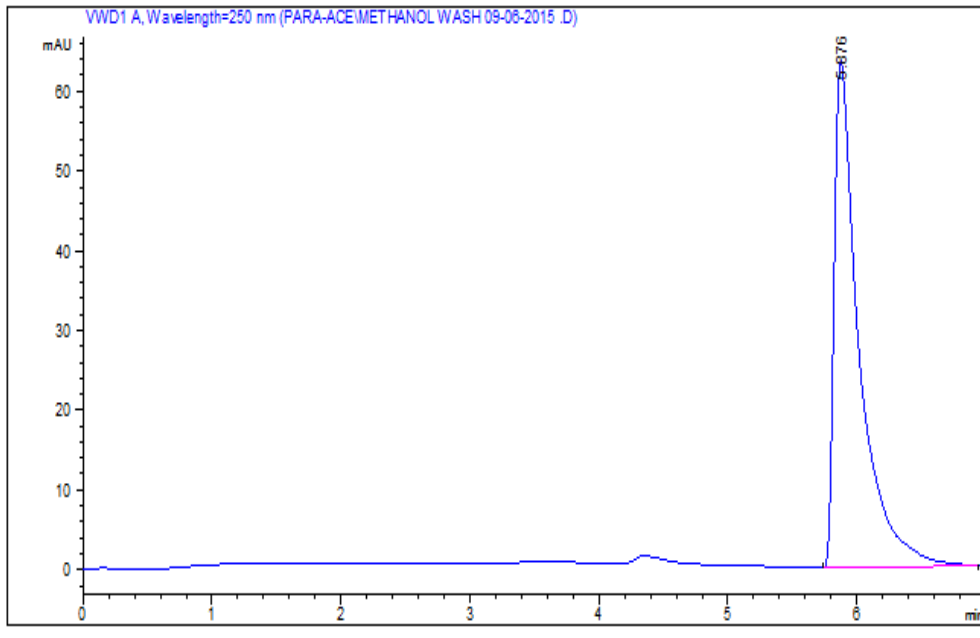
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

=====
Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 5% 08-10-2015



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.876	BB	0.1921	855.29620	63.50772	100.0000

Totals : 855.29620 63.50772

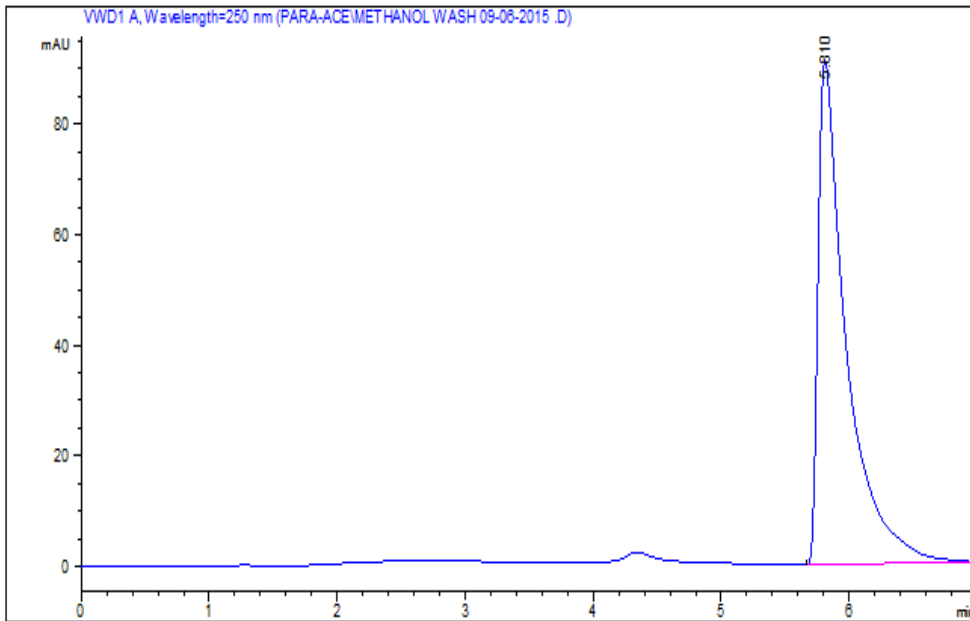
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 104 08-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.810	BB	0.2159	1401.71912	91.14816	100.0000

Totals : 1401.71912 91.14816

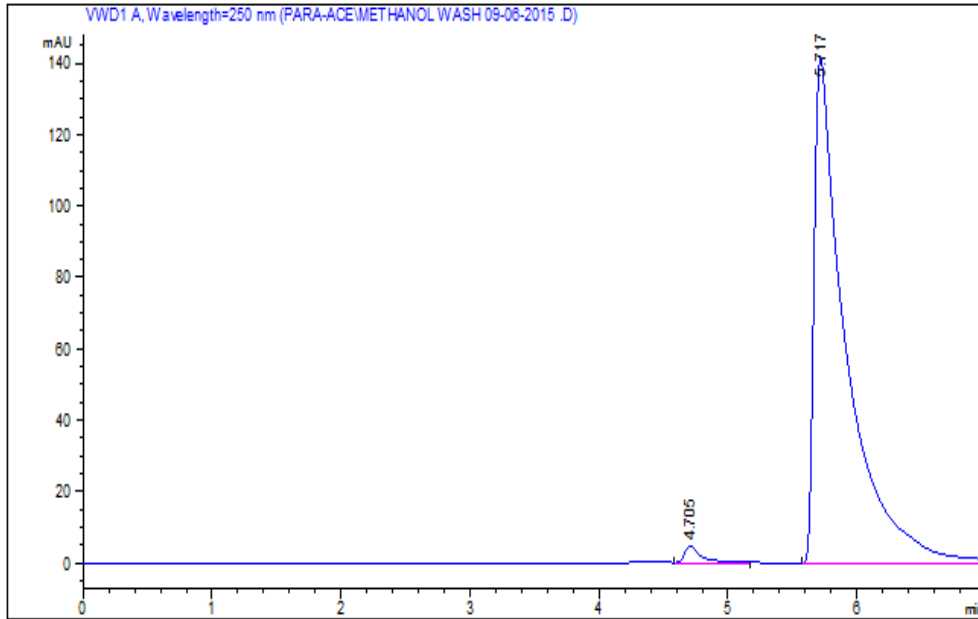
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 20% 08-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.705	VB	0.1282	42.64478	4.81073	1.7322
2	5.717	BBA	0.2304	2419.25732	141.25519	98.2678

Totals : 2461.90210 146.06591

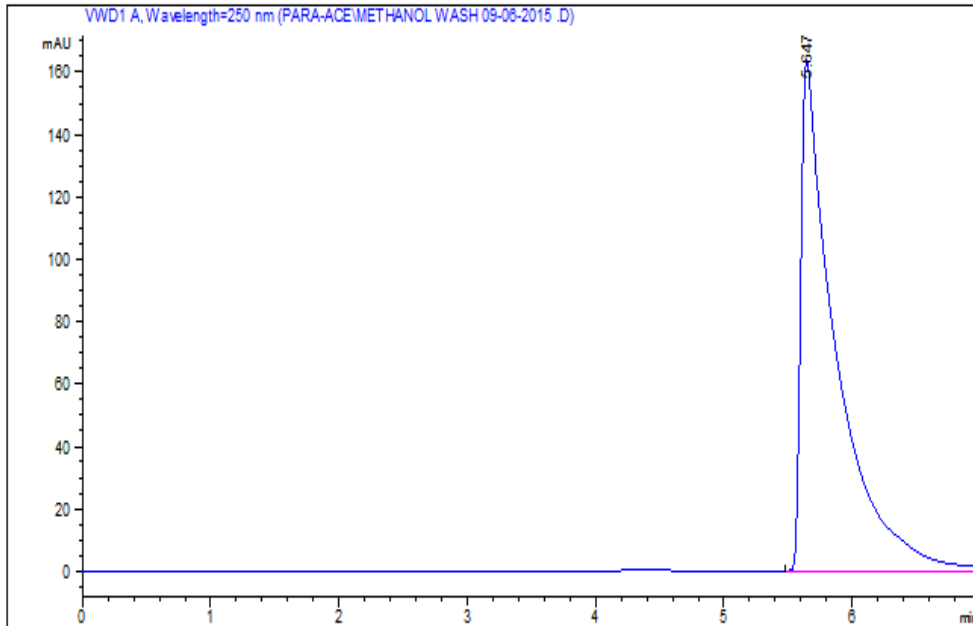
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 30% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.647	BBA	0.2474	3084.15845	163.79189	100.0000

Totals : 3084.15845 163.79189

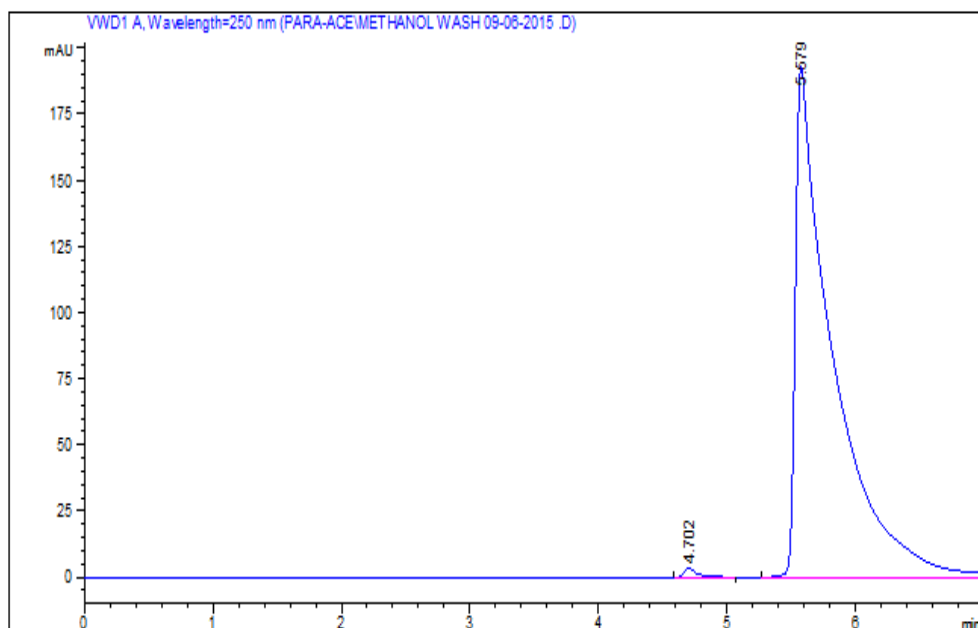
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 40% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.702	BB	0.1188	28.22420	3.44725	0.7241
2	5.679	BBA	0.2574	3869.84619	192.89835	99.2759

Totals : 3898.07039 196.34560

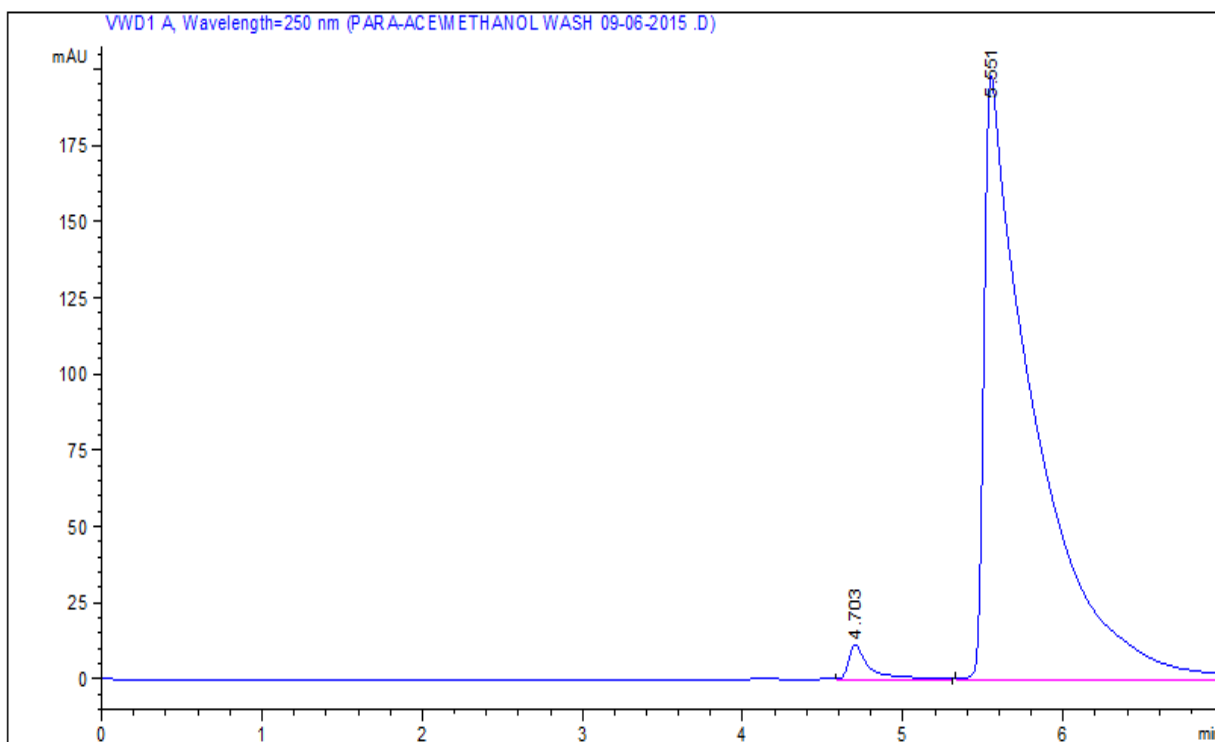
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 50% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.703	BB	0.1288	101.60952	11.23609	2.3349
2	5.551	BBA	0.2737	4250.18066	198.05289	97.6651

Totals : 4351.79018 209.28898

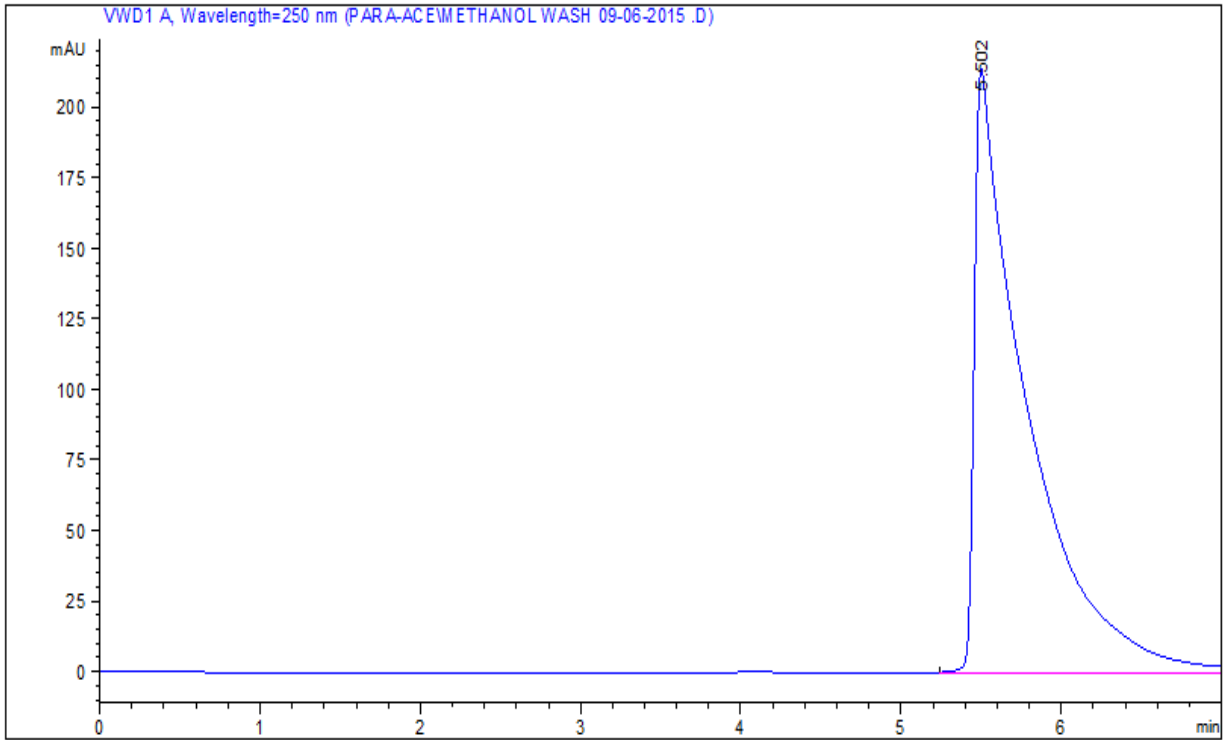
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 60% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.502	BBA	0.2848	4826.10400	214.10268	100.0000

Totals : 4826.10400 214.10268

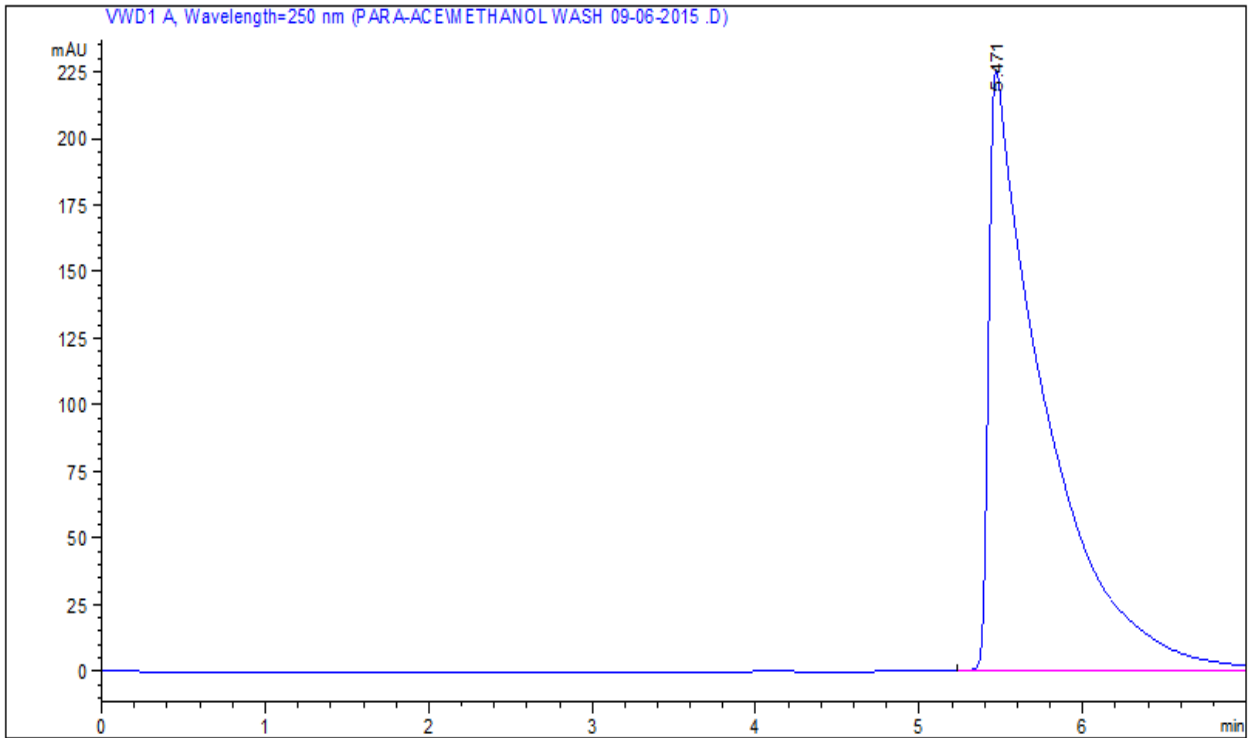
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 70% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.471	BBA	0.3012	5357.10645	226.06956	100.0000

Totals : 5357.10645 226.06956

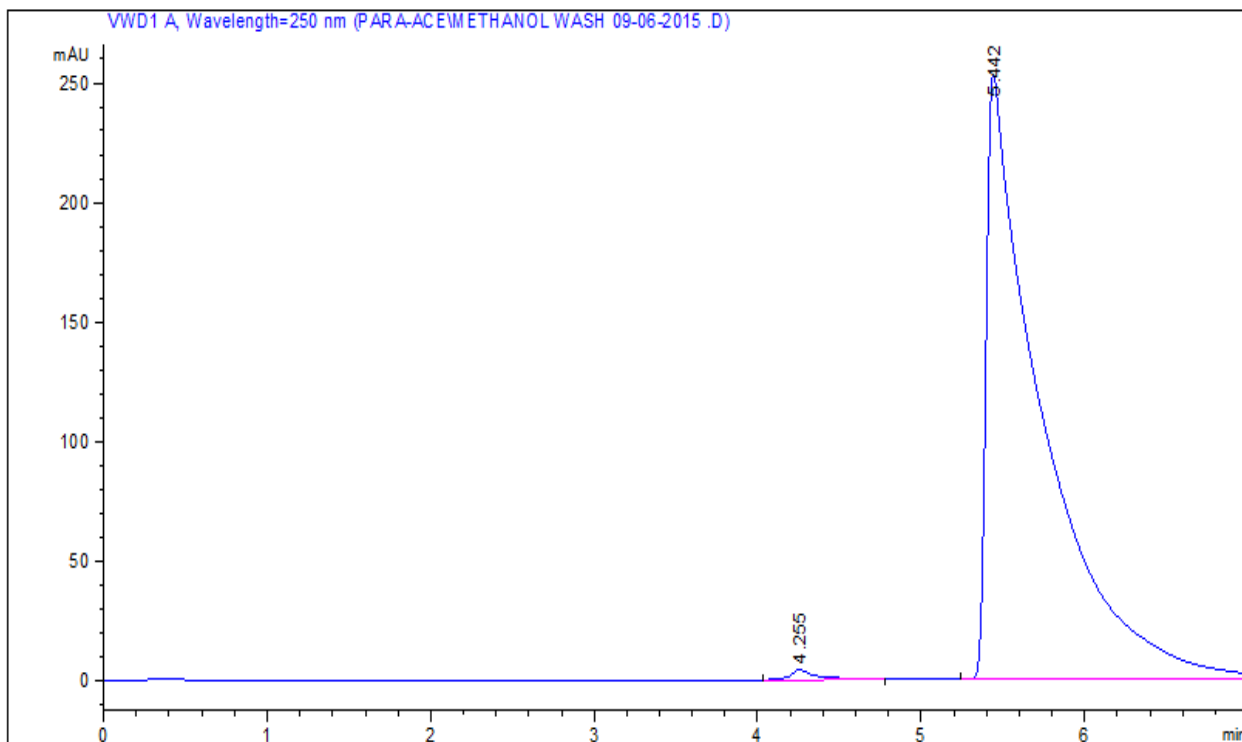
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: 80% 08-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.255	BB	0.1487	48.44927	4.40526	0.8047
2	5.442	BBA	0.2995	5971.99658	253.58334	99.1953

Totals : 6020.44585 257.98860

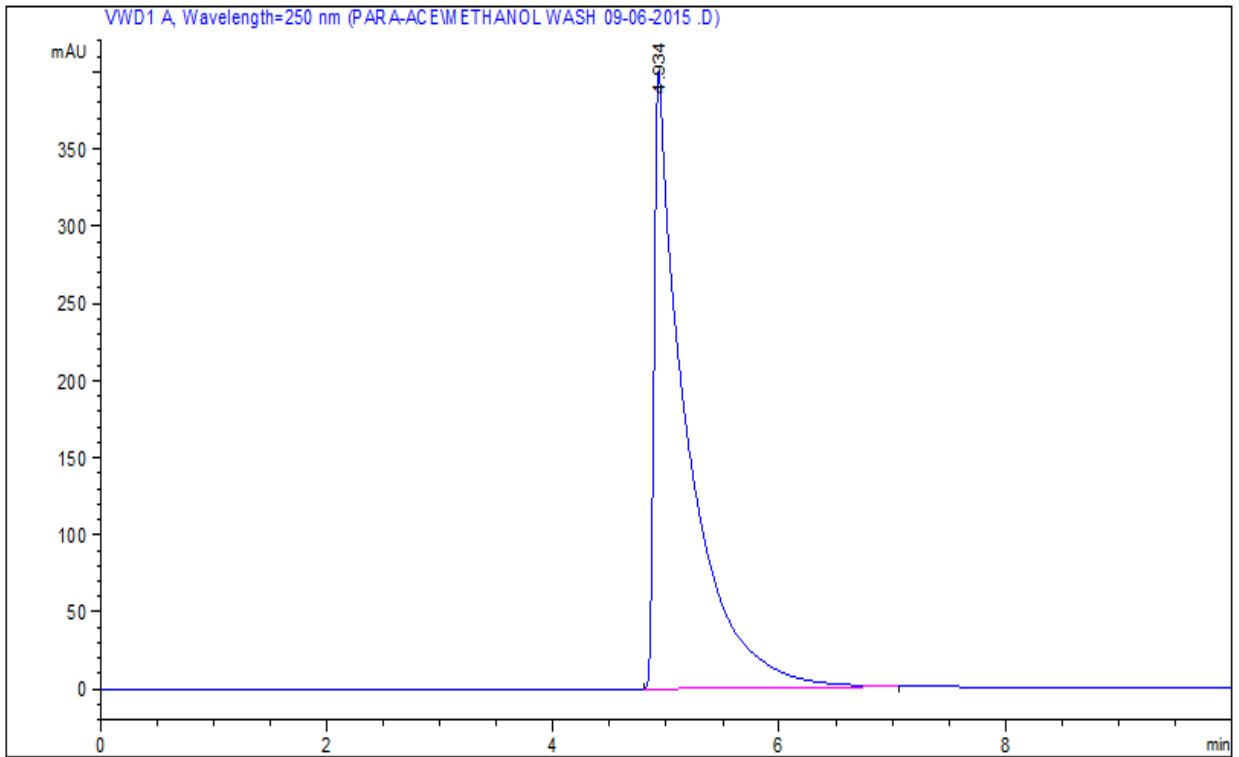
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: formic acid 100% 21-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.934	BB	0.2510	7919.52295	400.75348	100.0000

Totals : 7919.52295 400.75348

=====
Summed Peaks Report
=====

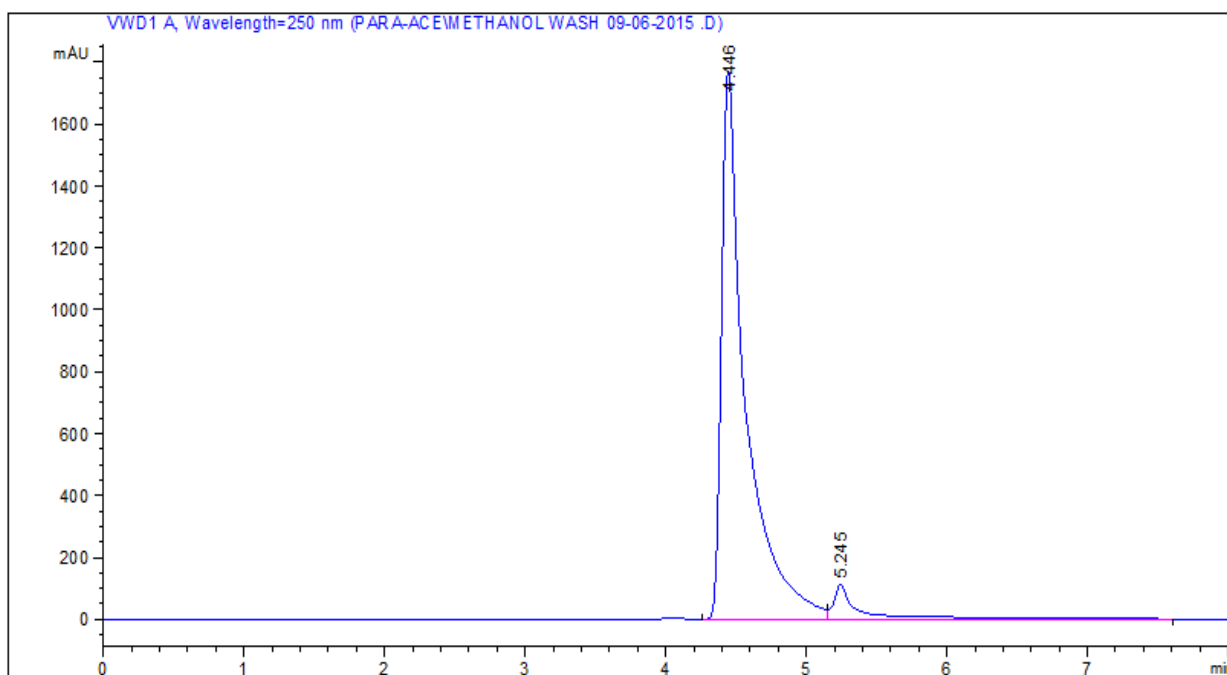
Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Annexure B

Sample Name: catalyst 5 min 21-10-2015



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.446	VV	0.1646	2.10201e4	1772.55872	93.4496
2	5.245	VB	0.1676	1473.40747	114.50569	6.5504

Totals : 2.24936e4 1887.06441

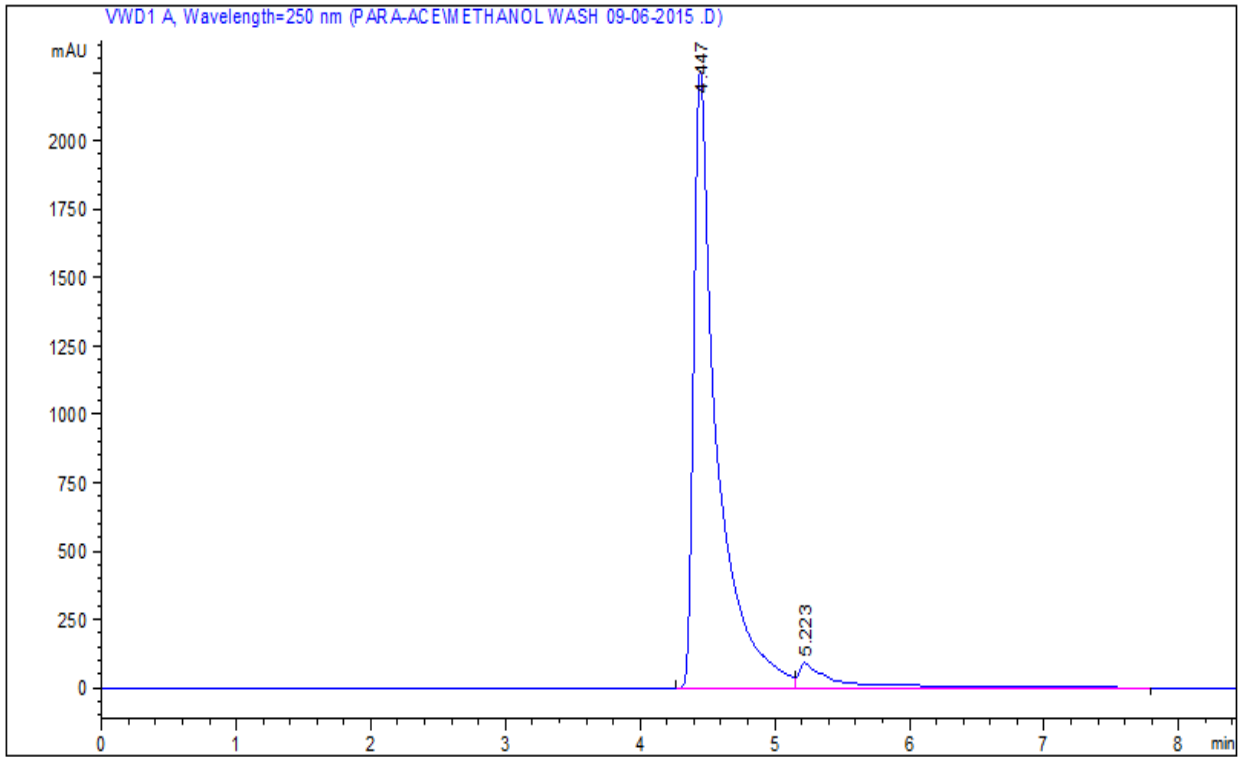
Summed Peaks Report

Signal 1: VWD1 A, Wavelength=250 nm

Final Summed Peaks Report

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 10min 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.447	VV	0.1648	2.68030e4	2257.03516	93.7502
2	5.223	VB	0.2476	1786.80664	91.18583	6.2498

Totals : 2.85898e4 2348.22099

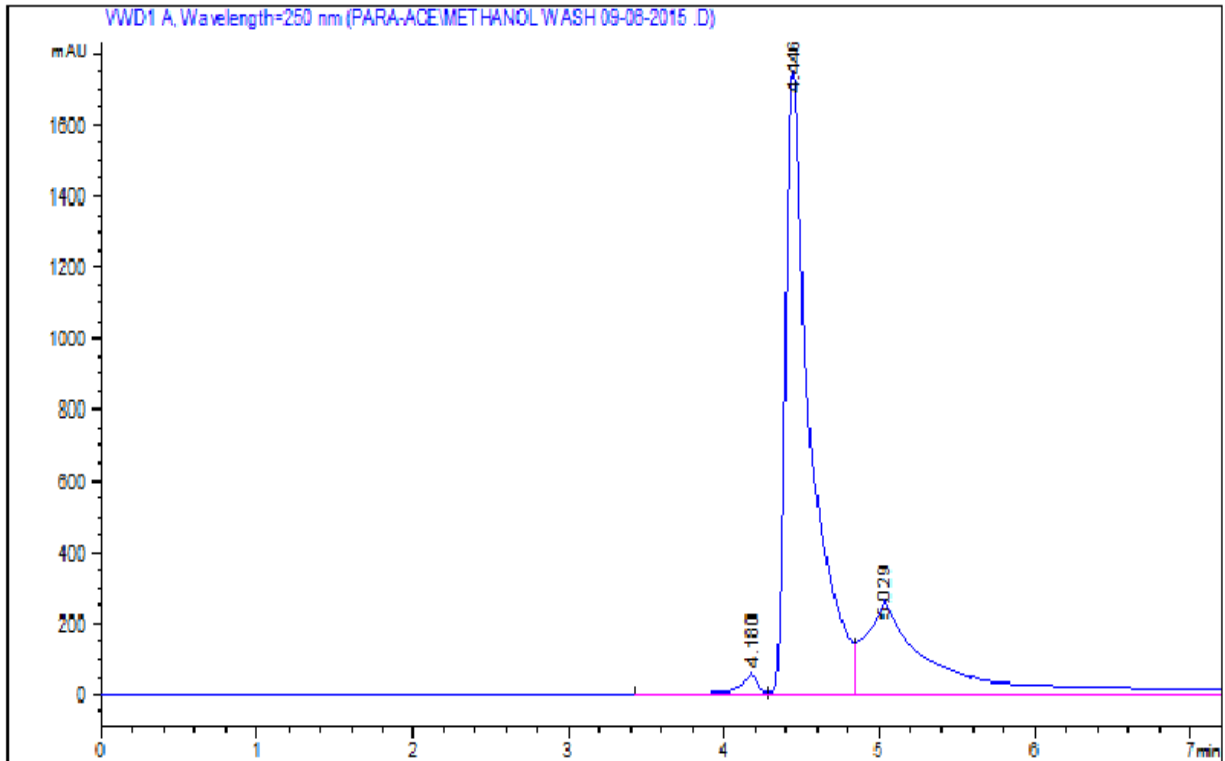
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 20 min. 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

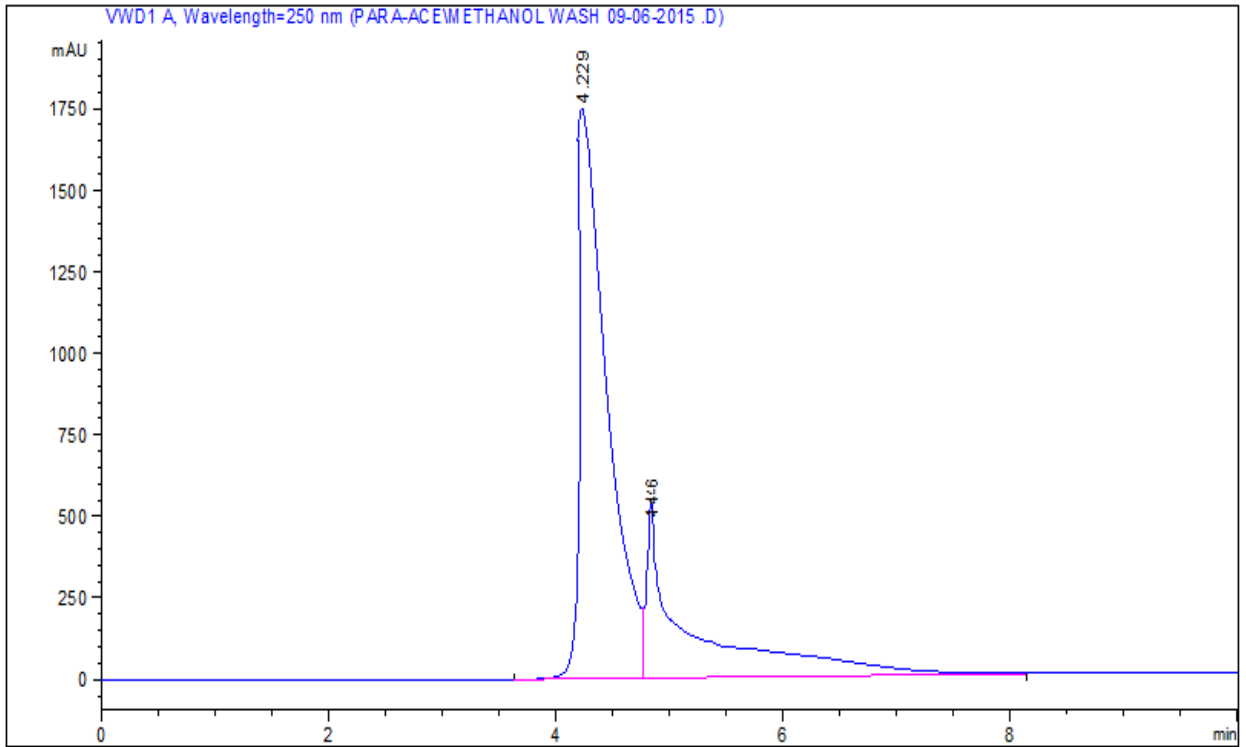
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.180	BV	0.1111	453.58789	57.40260	1.5661
2	4.446	VV	0.1567	1.95684e4	1750.18884	67.5650
3	5.029	VBA	0.6558	1894.53725	194.49751	30.8688

Totals : 2.89623e4 2002.08895

=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 45 min 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.229	EV	0.2477	3.54319e4	1866.52148	81.4041
2	4.446	VB	0.1247	4332.11426	489.10977	18.5959

Totals : 3.87640e4 2255.63126

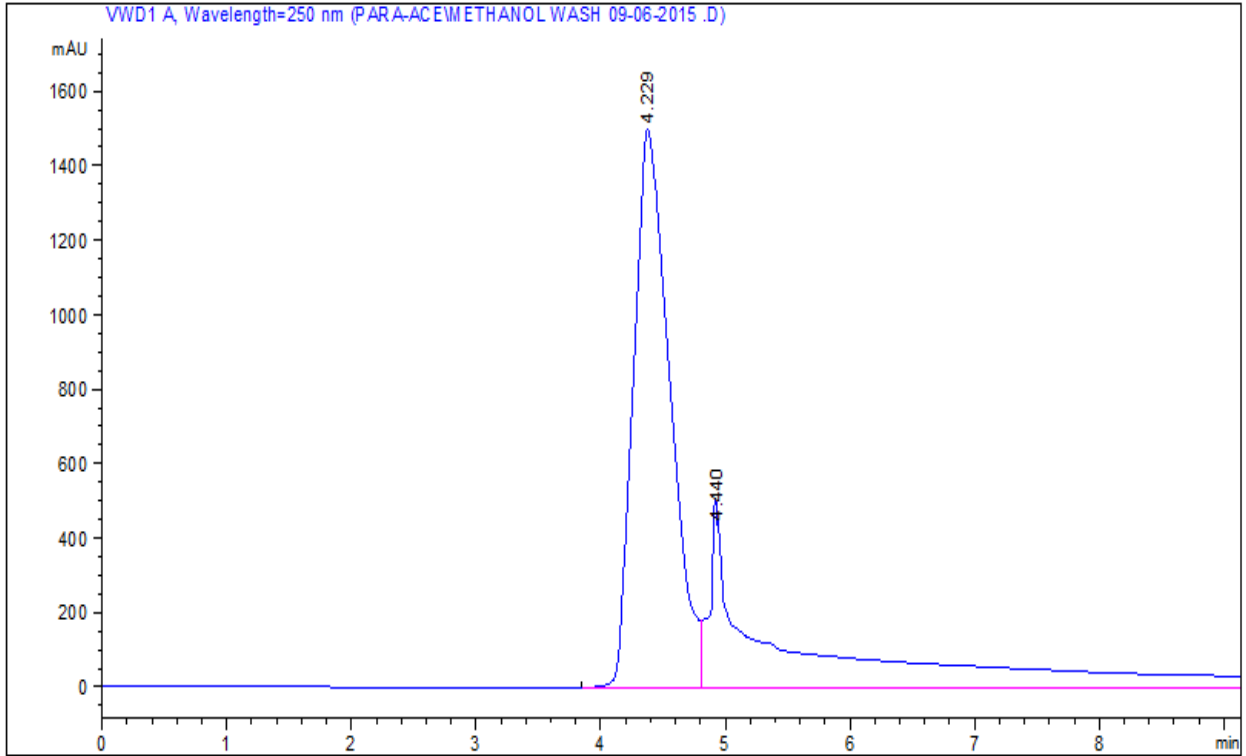
=====
Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 75 min 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.229	BV	0.4361	2.66599e4	1663.47363	69.3120
2	4.440	VV	0.1229	4997.96118	482.73804	31.7935

Totals : 2.49486e4 2902.37305

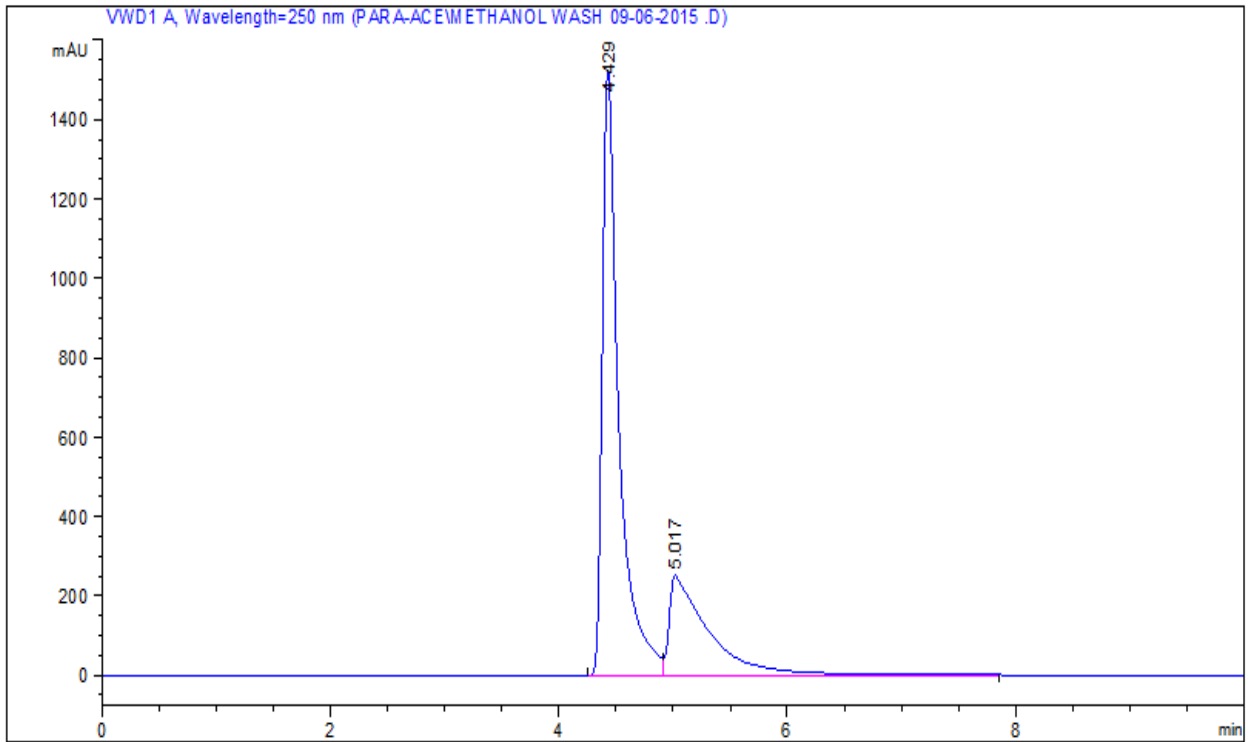
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 2h xx 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.429	BV	0.1457	1.54412e4	1527.16833	71.8137
2	5.017	VB	0.3044	6060.55566	251.51189	28.1863

Totals : 2.15017e4 1778.68022

=====
Summed Peaks Report
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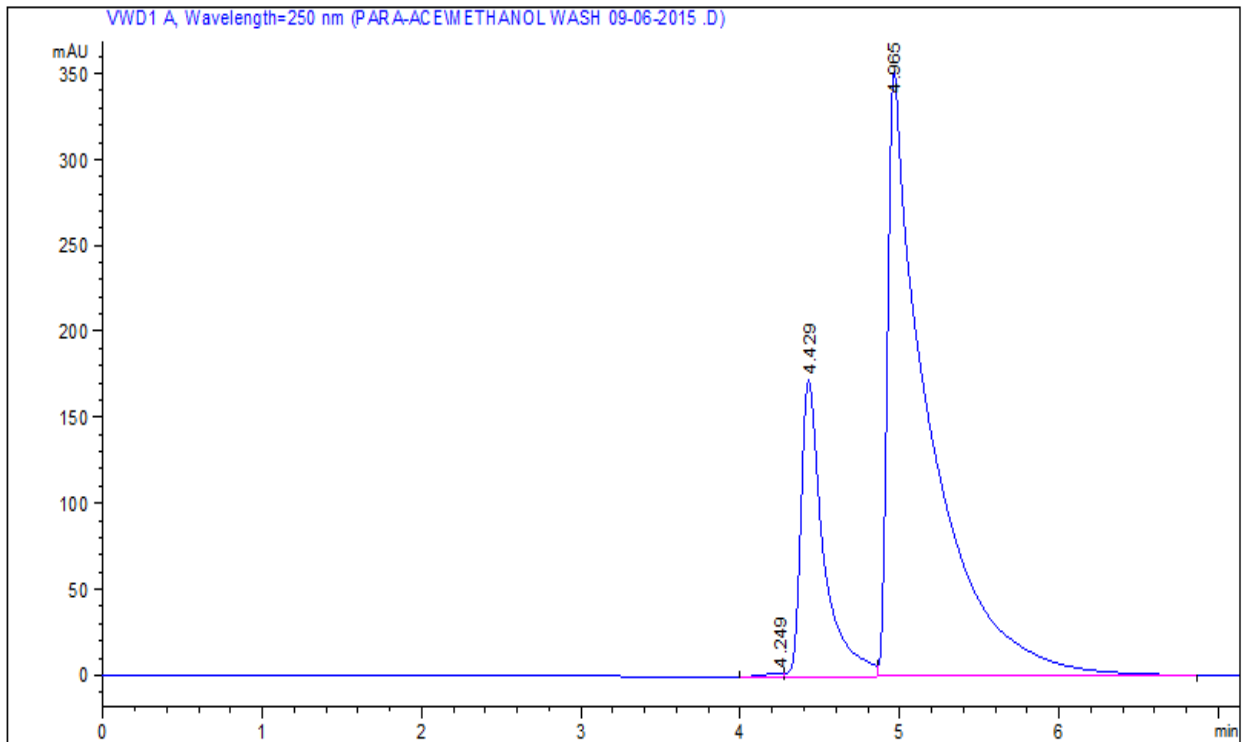
Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 2.5h xx 21-10-2015



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Area Percent Report
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Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.249	BV	0.1294	16.69815	2.06344	0.2068
2	4.429	VV	0.1431	1702.58765	172.13400	21.0817
3	4.965	VB	0.2309	6356.87256	352.36749	78.7116

Totals : 8076.15836 526.56494

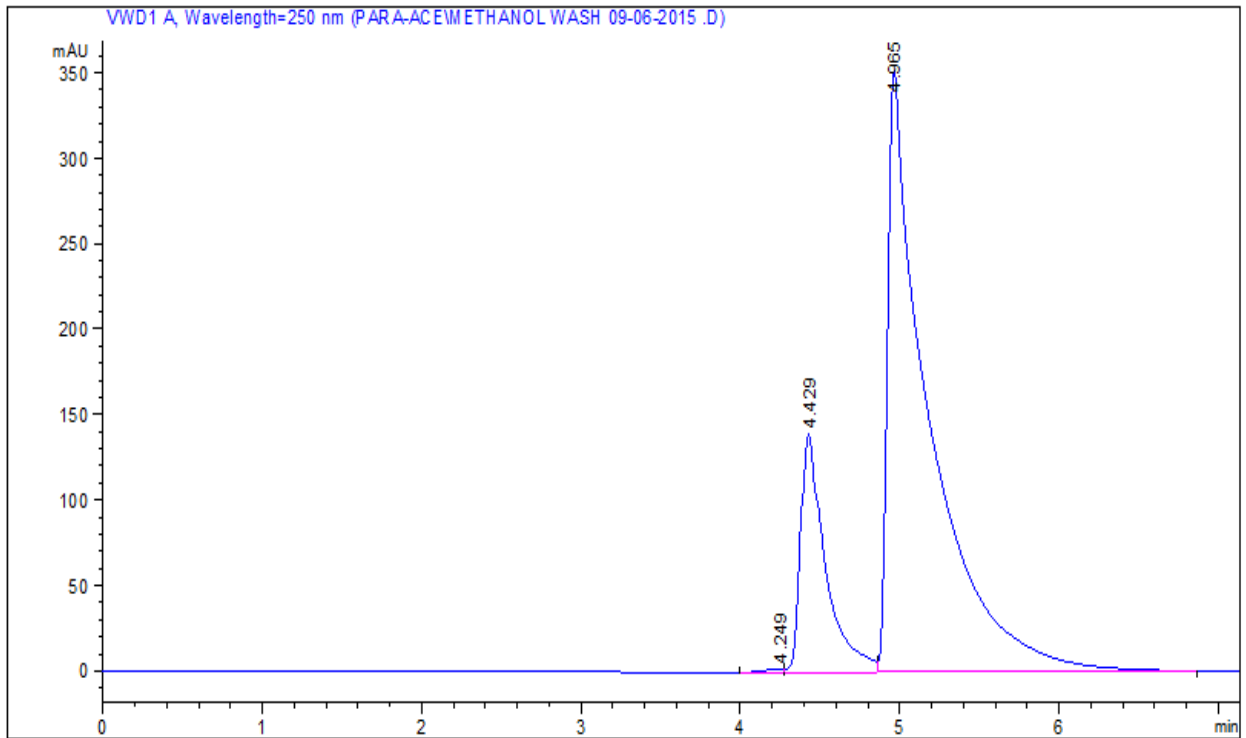
=====
Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
=====

Signal 1: VWD1 A, Wavelength=250 nm
Signal 1: VWD1 A, Wavelength=250 nm

Sample Name: catalyst 3 h xx 21-10-2015



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Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=250 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.249	BV	0.1294	10.69815	2.06344	0.2068
2	4.429	VV	0.1431	1400.58765	150.13400	21.0817
3	4.965	VB	0.2309	6560.87256	352.36749	78.7116

Totals : 8076.15836 526.56494

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Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm

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Final Summed Peaks Report
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Signal 1: VWD1 A, Wavelength=250 nm
Signal 1: VWD1 A, Wavelength=250 nm