Paraffin Oxidation Studies

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***Abstract* – The oxidation of paraffin has been studied with keen interest by several workers from all over the world; as oxidation leads to the introduction of various functional groups in hydrocarbon chains. Processes involving the Oxidation of Paraffin's in the liquid phase, using air or oxygen are of great importance to industrialized economies because of their role in converting petroleum hydrocarbon feed stocks such as alkanes, olefins and aromatics into industrial organic chemicals important in the polymer, petrochemicals ,cosmetics and detergent industries.**

The oxidation leads predominantly to the formation of secondary alcohols consisting of a mixture of all possible isomers with the same number of carbon atoms in the molecules as the initial hydrocarbons. The secondary alcohols which are oxidation products of paraffin exhibit excellent hydrolytic, oxidative and color stability, because of the nature of their branching. These alcohols have lower melting points than straight chain alcohols of corresponding length, while retaining their high temperature stability. The oxidation of paraffin wax to fatty acids is carried out in temperature range 110 ^{0}C- 140 ^{0}C.

Paraffin oxidation which is carried out by ALFOL, Oxo-processes, are high temperature, high pressure processes which utilize expensive catalysts, making them energy intensive as well as expensive. The maximum conversion achieved yet by existing processes is 15% for a batch time of 4 hours. A cheaper alternative in this article has been studied, in which paraffin Oxidation has been carried out in a foam reactor at moderate temperature and pressure with suitable catalyst , the output of the products is increased up to 62%.

***Keywords* – Paraffin Oxidation, Catalyst, Foam Reactor.**

INTRODUCTION

The oxidation of paraffin has been the keen interest by several workers from all over the world; as the oxidation leads to introduction of various functional groups in hydrocarbon chains, even in saturated ones. Liquid phase oxidation of paraffin wax to fatty acids was first exploited in Germany to replace partly the import of fats during Second World War,Since then the process has been successfully commercialized in several countries like U.S.A, U.S.S.R, and East Germany. [1]

Company like Petrolite Corporation and Alox Corporation manufacture a wide range of oxygenated hydrocarbons. These products are produced by the controlled liquid phase partial oxidation of various petroleum fractions. Normally these oxides are mixtures of organic acids.;oxy acids etc.They vary from one another in molecular weight (determined by raw material selected). and esters of oxidation. These oxidates are used in rust preventives, oil soluble lubricating agents, emulsifiers, or demulsifies, corrosion inhibitors etc.

Many processes were developed to manufacture fatty acids of various molecular weights. The manufacture of higher fatty alcohols; which have potential uses as starting material for the manufacturing of lubricating oil, additives, synthetic lubricating oil, plasticizers and others. A more selective process for the oxidation of paraffin to alcohols has been conducted by Bashkirov , khim and co workers; who conducted the reaction in the presence of Boric acid. The alcohols are stabilized in the form of their esters; which are resistant to further oxidation and hence very high selectivity is achieved.[2,3]

Paraffin oxidation mechanism

1st stage
Hydrocarbon → Hydro peroxide

2nd stage
Hydro peroxides → ketones → acids

↕↕ ↑ *Alcohols*

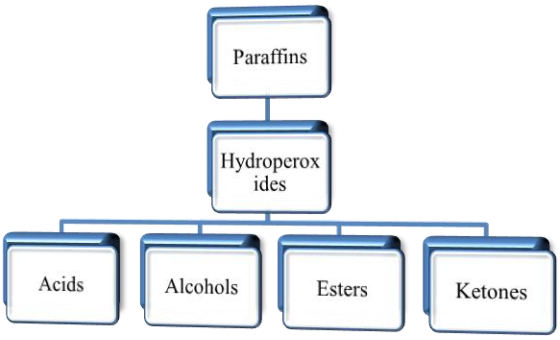

Fig.1. Paraffin Oxidation Mechanism

The oxidation leads predominantly to the formation of secondary alcohols consisting of a mixture of all possible isomers with the same number of carbon atoms in the molecules as the initial hydrocarbons.

The secondary alcohols which are of oxidation products of paraffin exhibit excellent hydrolytic ,oxidative and co lour stability because of the nature of their branching; These alcohols have lower melting points than straight chain alcohols of corresponding length while retaining their high temperature stability. Their possible applications are as alcohol sulphates or ether sulphates for use in detergents, cosmetics and industrial processes as ethoxylates or propoxylates as non-ionic surfactants for a wide variety of industrial uses as esters for lubricants, emulsifiers, antioxidants, polymers, alkyl halides, amines and ether amines used as petroleum additives and alcohol themselves as emulsifiers, solublizers, antifoams etc. [4]

AVAILABLE TECHNOLOGIES

The oxidation of paraffin wax to fatty acids is normally carried out in temperature range 110 ^{0}C- 140 ^{0}C$^{.}$ In the reaction, the effect of mass transfer can be eliminated by keeping sufficiently high value of air flow rate initially.

Nesmelov and coworkers **[6]** have reported significant improvement in yield and quality of fatty acids by continuous foam phase oxidation. And recommended use of 5 %alcohol from sperm whale oil along with soda ash to obtain homogeneity in foam phase. Higher conversion levels beyond 50 % leads to the formation of more of more oxygenated and water soluble acids and hence the oxidation is stopped when the degree of conversion is between 30 to 50 %.

Paraffin oxidation which is carried out by ALFOL, Oxo-processes, are high temperature, high pressure processes which utilize expensive catalysts, making them energy intensive as well as expensive. The maximum conversion achieved yet by existing processes is 15% for a batch time of 4 hours. The rate of oxidation may be increased by increasing the inter -facial area by Foam in a reactor, where we can get significant improvement in the yield and quality of fatty acids by continuous foam.

Extensive information is available regarding paraffin oxidation mechanism. However; most of the information’s are relevant for paraffin oxidation processes. and its studies in batch and continuous operations, Very little information is available for the paraffin oxidation studies in foam reactor.

A cheaper alternative in this paper has been studied, in which paraffin Oxidation has been carried out in a foam reactor at moderate temperature and pressure with suitable catalyst , the output of the products are increased up to 62%.[5,7,8].

METHODOLOGY

The major products of paraffin oxidation are

1. Fatty Acids 2. Fatty Alcohols
3. Esters 4. Aldehydes and Ketones

Fatty acid concentration equal or higher than 1 mM may be easily determined by titrimetry, .Titrimetry was classically used to determine the acid value (free fatty content) of vegetable oils and fats. This acid value is defined as the number of mg of KOH required to neutralize.

The Fatty acids. Contained in 1 gm of fat.

*The acid value is calculated by formula = 56.1*N*V/M*

Where V is the number of ml of KOH solution used N is exact normality, M is the mass in gm of sample.

The complete product analysis has been carried out by modern analytical tool like, GC-Mass Spectrophotometer.

*GC–MS Details:-*The gas chromatograph is equipped with a flame –ionization detector maintained at a temperature of about 260, a split less injection system, and a 0.53 mm * 30m fused silica capillary column bonded with a 1.0 km layer of phase G16.The chromatograph is programmed to maintain column temperature at 700c for about 2 minutes after injection ,then to increase the temperature at the rate of 5 per minute to 240 and finally to maintain its temperature for 5 minutes .The injection port temperature is maintained at about 220,the carrier gas is helium with a linear velocity of about 50 cm per second. Chromatographs are in terms of absorbance vs retention time.

EXPERIMENTAL DETAILS

The foam reactor used in the present experimental work was a laboratory scale reactor similar to that described by Bashkirov and Solviet process, having 6.38 cm diameter; and100cm length. Reactor has been made from glass; advantage is non-corrosive in nature, transparent, and resistant to many chemicals. Glass reactors were packed with packing material, rasching rings, up to 15 cm height; size of rasching rings 12*12 mm,. For measuring flow rates, rota meters were installed at the inlet for both air and water. having Range (1-250 lpm) .Paraffin oil was heated in SS vessel having capacity 5lits.SS vessel was provided with internal cladding of alumina with internal heater (0-200^{o}c) and temperature indicator. Samples after oxidations were collected in a flask having capacity 250 ml.

Experimental Procedure:-

The initial temperature has been maintained between 130-170 °C.

The air flow-rate has been maintained between 1-5 litres per minute and water flow rate, one lit/min.. The catalysts used were: Boric acid; Potassium permanganate; Magnesium Oxide. The concentration of the catalyst has been kept between 5-10%.

The surfactant used was Sodium laurel sulphate. in a slurry form, Concentration was kept max 5 % by weight.

Chemicals used: **-** Paraffin oil, a combination of catalyst such as magnesium Oxide (MgO), Potassium paramaganet (KMnO$_{4)}$ and boric acid with different proportions.

The reaction has been carried out for about 2, -5 hrs. The samples were collected at the interval of one hr. Samples were collected from bottom (50 ml app.) and were analyzed for acid contents by titration. The fatty alcohol analysis has been performed using GC -mass Spectrophotometer. Fatty acids contained in the alcohols were separated by Saponification and subsequent distillation. Alcohols have been set free by Hydrolysis. Primary alcohols were prepared by vacuum distillation. The bottom Products contained only secondary alcohols. Which were analysed by GC -mass Spectrophotometer. The product stream was separated into organic layer and aqueous layer using a separating funnel.

The properties of paraffin oil:-

1. Appearance: Clear colourless, viscous liquid.
2. Odour: Odourless
3. Solubility: Negligible (<0.1 %)
4. Specific gravity: 0.86-0.91
5. Volatiles by volume at 21°C: Nil
6. Melting Point: -18 to -25 °C
7. Vapour Pressure: <0.5 mm Hg at 20 °C
8. Flash Point: 220 °C

EXPERIMENTAL SET–UP

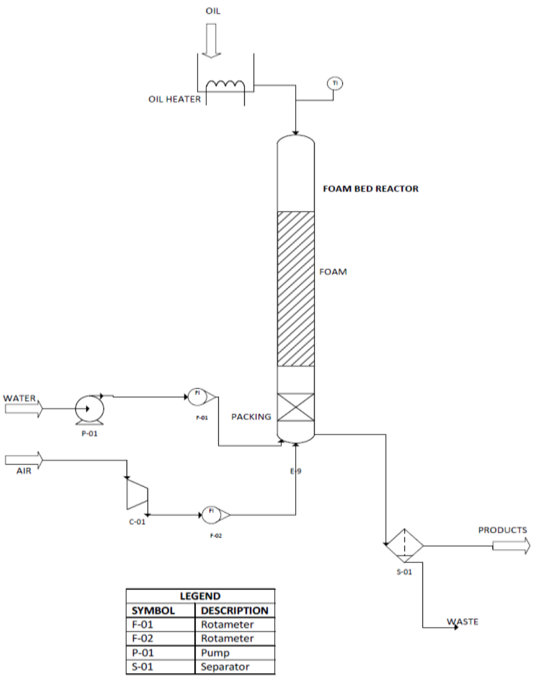

Fig.2. Experimental Set-up

RESULTS AND DISCUSSIONS

Fatty acids calculations are shown in Table no 1-5 with
Catalyst: Boric acid
Temperature range:- 130 ^{0}c,150 ^{0}c,170 ^{0}c
Samples were analyzed by titration at an interval of one hour.
Burette:-0.01N NaoH solution
Indicator 2to 3 drops of phenolphthalein
End point colourless to pink
Acid value =56.1*normality of burette solution*constant burette reading/total weight of sample

Table 1 : Pure paraffin oil acid value

Weight of oil gms	**Weight of ethyl alcohol added in excess gms**	**Total weight of sample gms**	**Burette reading**	**Acid value**
9gms	42.5gms	51.5gms	2.5ml	0.02723

Table 2 : Run no -1 Acid value

Run no	**Temp 0c**	**Time hr**	**Exact Weight of sample gms**	**Weight of ethyl alcohol gms**	**Total weight gms**	**Burette reading**	**Acid value**
1	130 0c	1hr	10.gms	20gms	30.gms	8,2ml	0.1508
		2hrs	10gms	20gms	30gms	8.9ml	o.1722
		3hrs	101gms	20gms	30gms	11.1ml	0.201

Table 3 : Run no -2 Acid value

Run no	**Temp 0c**	**Time hr**	**Exact Weight of sample gms**	**Weight of ethyl alcohol**	**Total weight**	**Burette reading**	**Acid value**
2	150 0c	1hr	12.5gms	28gms	40.5gms	11.5ml	0.153
		2hrs	12.5gms	28gms	40.5gms	16.8ml	0.2992
		3hrs	12.5gms	28gms	40.5gms	22.1ml	0.3306

Table 4 : Run No 3 Acid value

Run no	**Temp 0c**	**Time hr**	**Exact Weight of sample gms**	**Weight of ethyl alcohol gms**	**Total weight gms**	**Burette reading**	**Acid value**
3	170 0c	1hr	12.5gms	28gms	40.5gms	14.5ml	0.2008
		2hrs	12.5gmsgms	28gms	40.55sgms	20.8.8ml	0.2954
		3hrs	12.5gms	28gms	40.5gms	24.1.ml	0.3863

Table 5 : Summary of run 1-3 for Fatty acids

Run No.	**Temperature (°C)**	**Acid Value (mg of KOH)**		
		Time = 1 hour	**Time = 2 hours**	**Time = 3 hours**
1	130	0.1508	0.1722	0.201
2	150	0.1593	0.2292	0.3306
3	170	0.2008	0.2954	0.3863

Table 6 : Fatty alcohols Analysis is done by GCMS
(GCMS 5-9) GCMS are marked with figure. Refer Fig (GCMS 5-9)

Run No	Catalyst	Wt of aqueous layer gms	Wt of organic layer gms	Area in GCMS %	Wt of useful product gms	Con-version %	Products after oxidation (listed from GCMS compounds)
4	$KMNO_4$	940gm	1220gm	32.3%	394.06	32.8	6-Octadecenoic acid, 9-Octadecenoic acid, 5-Octadecenoic acid; Phosphonic acid, 1-Butanone, 1-Nonanol, Carisoprodol
5	MgO	900gms	1260gms	16.1%	144.9gms	12.1	6-0ctenal,1-Heneicosylformate, 4-Hexan-1-ol, Cyclohexaneehanol, Aspidospemidin-17-ol
6	MgO + $KMNO_4$	950gms	1210gms	62.3%	753.9gms	62.83	1-Docosanol, 2-Butanone, Longifoneldehyde, cyclopropanenoanoic acid
7	Boricacid + MgO + $KMNO_4$	940gms	1220gms	35.3%	430.66gms	35.88	Tricosyl formate, Hexenoic acid, Hetadecanol

DISCUSSIONS

Fatty acids were produced the most, when using Boric acid as a catalyst. (Fig no- 3), Acid conversion increases with temperature; it is highest (0.3863), at a temp of 170 0c.(table no-5).

From table No-6, we can observe that, the major products are Fatty alcohols, acids, esters, aldehydes and ketones. Hence paraffin oxidation by foam reactor is viable.

According to available information, the maximum conversion achieved yet by existing processes is 15% for a batch time of 4 hours. Using a catalyst combination of Magnesium oxide and Potassium permanganate, the conversion achieved is about 62%(fig no-4) . This is much higher than the available information.

Paraffin oxidation in a foam reactor is a superior than paraffin oxidation in a batch reactor. The existing process, for example the ALFOL process or Oxo-process use high temperatures and pressures for conversion of paraffin oil to fatty alcohols and acids. The method proposed, oxidation in foam reactor provides, an alternative, which is less energy intensive as compared to the existing process.

The product stream formed is mixture of a large variety of products. Separation is required to utilise fatty alcohols or fatty acids in cosmetics, emulsifiers and thickeners and other given applications.

CONCLUSION

We can conclude that the paraffin oxidation in a foam reactor is a better alternative method than paraffin oxidation in a batch reactor.

The existing process, for example the ALFOL process or Oxo-process use high temperatures and pressures for conversion of paraffin oil to fatty alcohols and acids.

The method proposed oxidation in foam reactor provides, an alternative, which is less energy intensive as compared to the existing processes.

The maximum conversion achieved yet by existing processes is 15% for a batch time of 4 hours. Using the right catalyst, a very high conversion of upto 62% has been achieved using foam-reactor for paraffin oxidation.

Fatty alcohols and acids form the majority of the product.The implementation of this process into a continuous process could be studied.

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AUTHOR'S PROFILE

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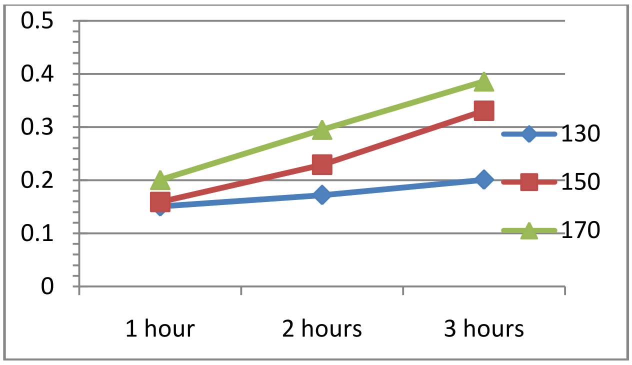

Fig.3. Acid Value versus Time at different Temperatures

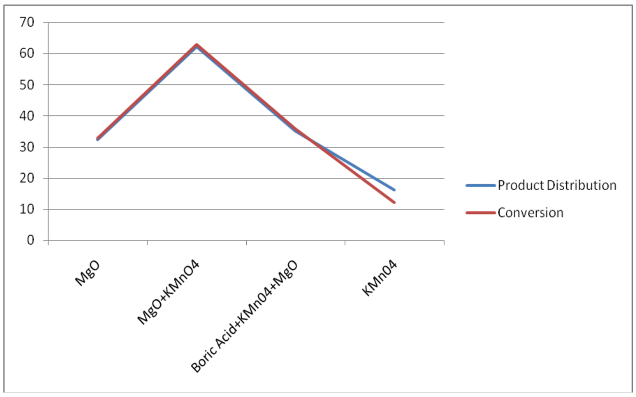

Fig.4. Effect of % conversion on catalyst with product distribution

Gas Chromatography/Mass Spectroscopy Results

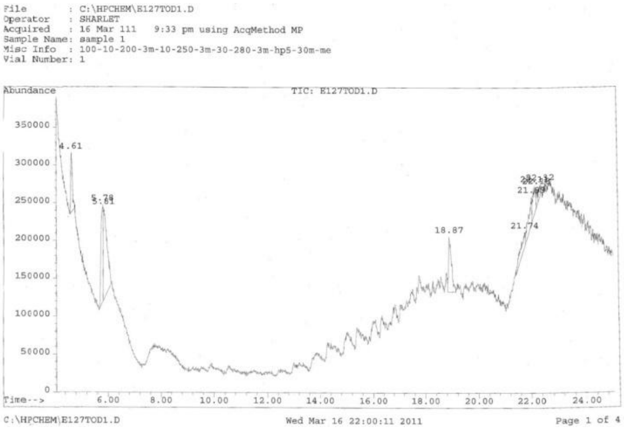

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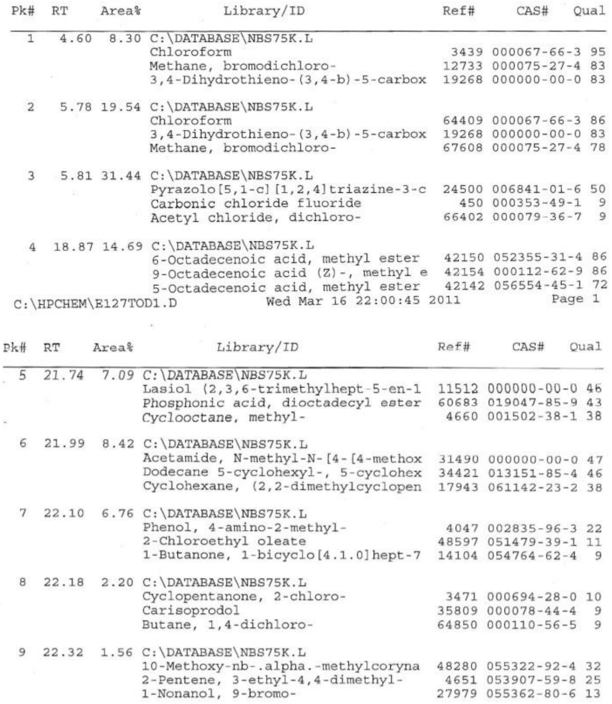
Fig.5. GCMS for paraffin oil

Compound for paraffin oil



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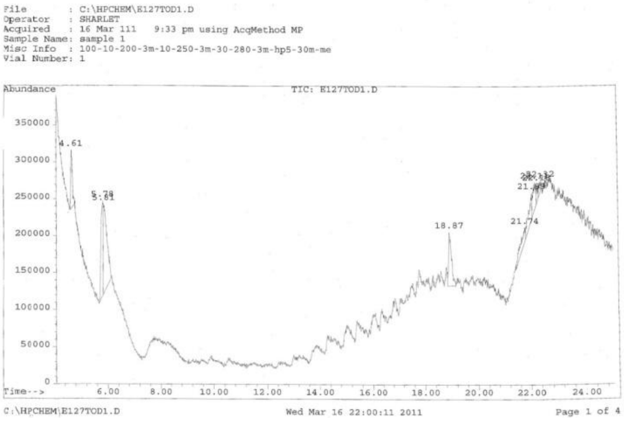

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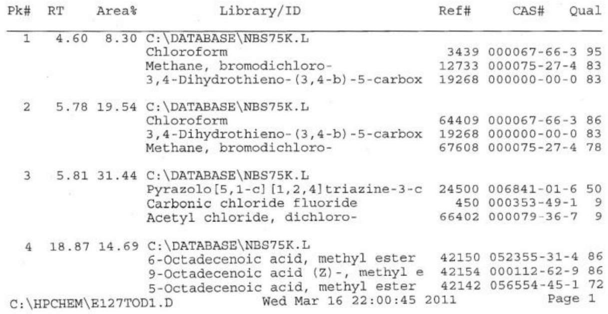
Fig.6. GCMS for catalyst $KMnO_4$

Compounds Formed for catalyst $KMnO_4$



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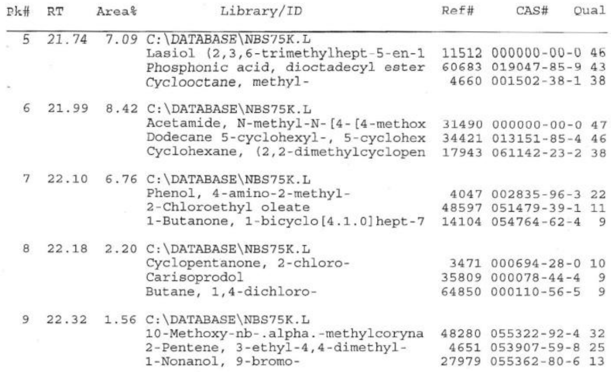

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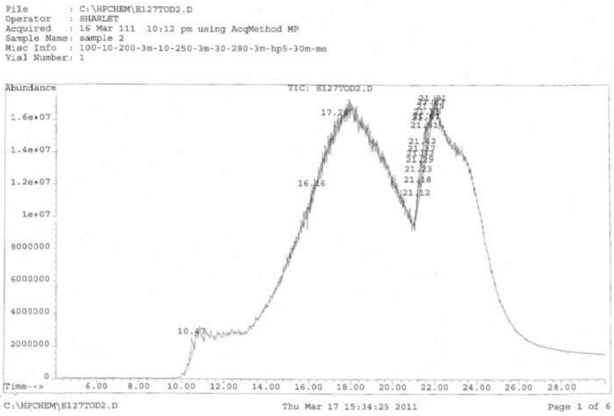

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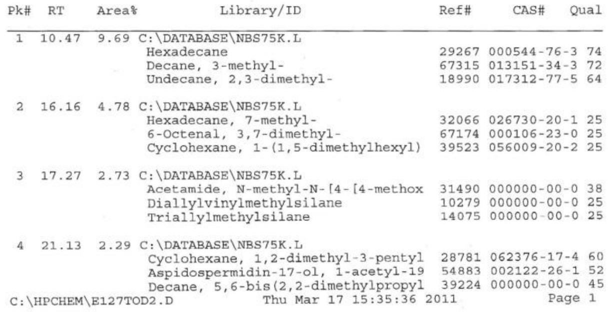
Fig.7. GCMS for catalyst MgO

Compound formed for catalyst MgO



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                  6-Octenal, 3,7-dimethyl-            67174 000106-23-0 25
                  Cyclohexane, 1-(1,5-dimethylhexyl)  39523 056009-20-2 25

  3  17.27  2.73 C:\DATABASE\NBS75K.L
                  Acetamide, N-methyl-N-[4-[4-methox  31490 000000-00-0 38
                  Diallylvinylmethylsilane            10279 000000-00-0 25
                  Triallylmethylsilane                14075 000000-00-0 25

  4  21.13  2.29 C:\DATABASE\NBS75K.L
                  Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 60
                  Aspidospermidin-17-ol, 1-acetyl-19  54883 002122-26-1 52
                  Decane, 5,6-bis(2,2-dimethylpropyl  39224 000000-00-0 45
C:\HPCHEM\E127TOD2.D          Thu Mar 17 15:35:36 2011          Page 1
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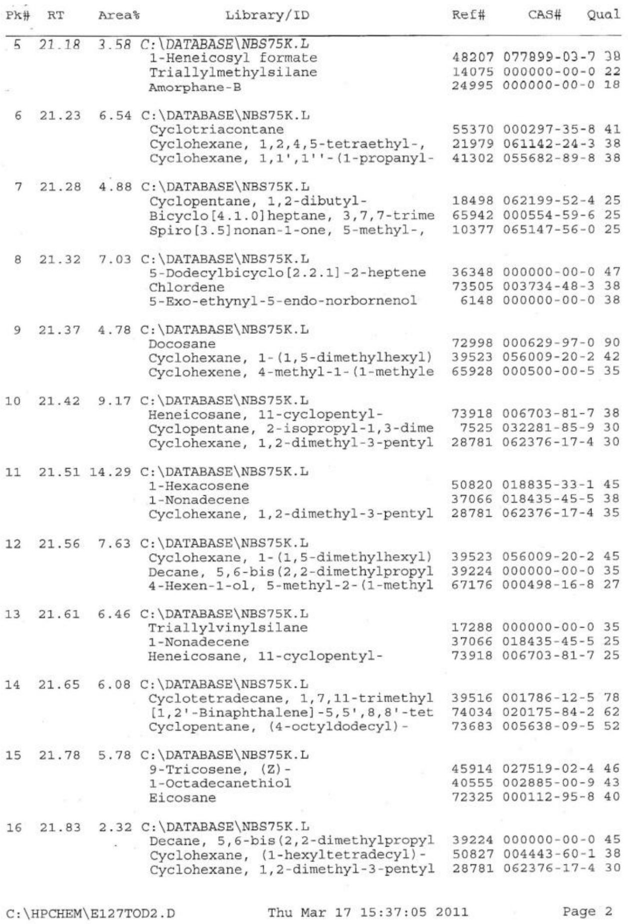

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                 1-Heneicosyl formate                48207 077899-03-7 38
                 Triallylmethylsilane                14075 000000-00-0 22
                 Amorphane-B                         24995 000000-00-0 18

 6  21.23  6.54 C:\DATABASE\NBS75K.L
                 Cyclotriacontane                    55370 000297-35-8 41
                 Cyclohexane, 1,2,4,5-tetraethyl-,   21979 061142-24-3 38
                 Cyclohexane, 1,1',1''-(1-propanyl-  41302 055682-89-8 38

 7  21.28  4.88 C:\DATABASE\NBS75K.L
                 Cyclopentane, 1,2-dibutyl-          18498 062199-52-4 25
                 Bicyclo[4.1.0]heptane, 3,7,7-trime  65942 000554-59-6 25
                 Spiro[3.5]nonan-1-one, 5-methyl-,   10377 065147-56-0 25

 8  21.32  7.03 C:\DATABASE\NBS75K.L
                 5-Dodecylbicyclo[2.2.1]-2-heptene   36348 000000-00-0 47
                 Chlordene                           73505 003734-48-3 38
                 5-Exo-ethynyl-5-endo-norbornenol     6148 000000-00-0 38

 9  21.37  4.78 C:\DATABASE\NBS75K.L
                 Docosane                            72998 000629-97-0 90
                 Cyclohexane, 1-(1,5-dimethylhexyl)  39523 056009-20-2 42
                 Cyclohexene, 4-methyl-1-(1-methyle  65928 000500-00-5 35

10  21.42  9.17 C:\DATABASE\NBS75K.L
                 Heneicosane, 11-cyclopentyl-        73918 006703-81-7 38
                 Cyclopentane, 2-isopropyl-1,3-dime   7525 032281-85-9 30
                 Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 30

11  21.51 14.29 C:\DATABASE\NBS75K.L
                 1-Hexacosene                        50820 018835-33-1 45
                 1-Nonadecene                        37066 018435-45-5 38
                 Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 35

12  21.56  7.63 C:\DATABASE\NBS75K.L
                 Cyclohexane, 1-(1,5-dimethylhexyl)  39523 056009-20-2 45
                 Decane, 5,6-bis(2,2-dimethylpropyl  39224 000000-00-0 35
                 4-Hexen-1-ol, 5-methyl-2-(1-methyl  67176 000498-16-8 27

13  21.61  6.46 C:\DATABASE\NBS75K.L
                 Triallylvinylsilane                 17288 000000-00-0 35
                 1-Nonadecene                        37066 018435-45-5 25
                 Heneicosane, 11-cyclopentyl-        73918 006703-81-7 25

14  21.65  6.08 C:\DATABASE\NBS75K.L
                 Cyclotetradecane, 1,7,11-trimethyl  39516 001786-12-5 78
                 [1,2'-Binaphthalene]-5,5',8,8'-tet  74034 020175-84-2 62
                 Cyclopentane, (4-octyldodecyl)-     73683 005638-09-5 52

15  21.78  5.78 C:\DATABASE\NBS75K.L
                 9-Tricosene, (Z)-                   45914 027519-02-4 46
                 1-Octadecanethiol                   40555 002885-00-9 43
                 Eicosane                            72325 000112-95-8 40

16  21.83  2.32 C:\DATABASE\NBS75K.L
                 Decane, 5,6-bis(2,2-dimethylpropyl  39224 000000-00-0 45
                 Cyclohexane, (1-hexyltetradecyl)-   50827 004443-60-1 38
                 Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 30

C:\HPCHEM\E127TOD2.D           Thu Mar 17 15:37:05 2011           Page 2
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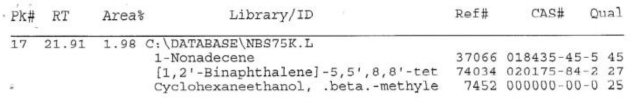

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                 [1,2'-Binaphthalene]-5,5',8,8'-tet  74034 020175-84-2 27
                 Cyclohexaneethanol, .beta.-methyle   7452 000000-00-0 25
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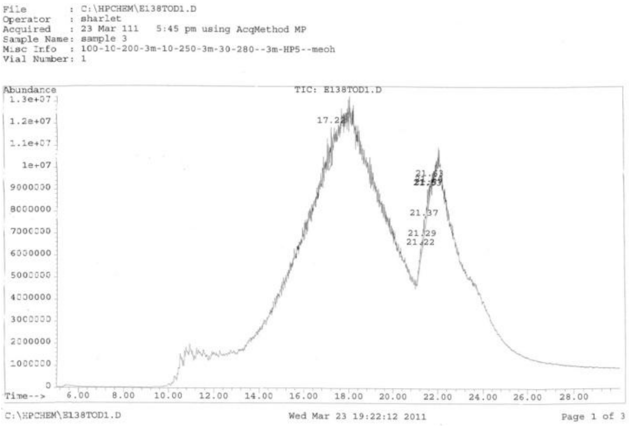

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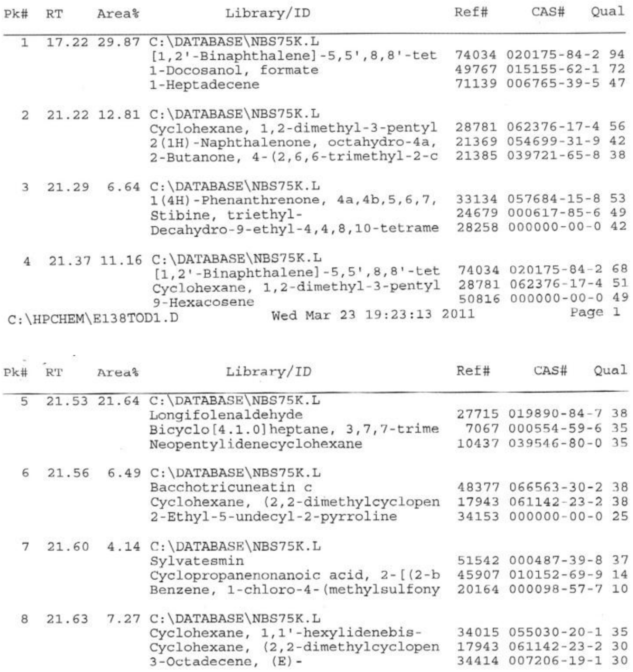
Operator    : sharlet
Acquired    : 23 Mar 111   5:45 pm using AcqMethod MP
Sample Name: sample 3
Misc Info   : 100-10-200-3m-10-250-3m-30-280--3m-HP5--meoh
Vial Number: 1
```

```
C:\HPCHEM\E138TOD1.D              Wed Mar 23 19:22:12 2011              Page 1 of 3
```

Fig.8. GCMS for Catalyst MgO and $KMnO_4$

Compound formed for catalyst MgOand KMnO$_4$



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                 [1,2'-Binaphthalene]-5,5',8,8'-tet  74034 020175-84-2 94
                 1-Docosanol, formate                49767 015155-62-1 72
                 1-Heptadecene                       71139 006765-39-5 47

  2  21.22 12.81 C:\DATABASE\NBS75K.L
                 Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 56
                 2(1H)-Naphthalenone, octahydro-4a,  21369 054699-31-9 42
                 2-Butanone, 4-(2,6,6-trimethyl-2-c  21385 039721-65-8 38

  3  21.29  6.64 C:\DATABASE\NBS75K.L
                 1(4H)-Phenanthrenone, 4a,4b,5,6,7,  33134 057684-15-8 53
                 Stibine, triethyl-                  24679 000617-85-6 49
                 Decahydro-9-ethyl-4,4,8,10-tetrame  28258 000000-00-0 42

  4  21.37 11.16 C:\DATABASE\NBS75K.L
                 [1,2'-Binaphthalene]-5,5',8,8'-tet  74034 020175-84-2 68
                 Cyclohexane, 1,2-dimethyl-3-pentyl  28781 062376-17-4 51
                 9-Hexacosene                        50816 000000-00-0 49
C:\HPCHEM\E138TOD1.D            Wed Mar 23 19:23:13 2011              Page 1

Pk#  RT     Area%             Library/ID                    Ref#      CAS#    Qual
-----------------------------------------------------------------------------------
  5  21.53 21.64 C:\DATABASE\NBS75K.L
                 Longifolenaldehyde                  27715 019890-84-7 38
                 Bicyclo[4.1.0]heptane, 3,7,7-trime   7067 000554-59-6 35
                 Neopentylidenecyclohexane           10437 039546-80-0 35

  6  21.56  6.49 C:\DATABASE\NBS75K.L
                 Bacchotricuneatin c                 48377 066563-30-2 38
                 Cyclohexane, (2,2-dimethylcyclopen  17943 061142-23-2 38
                 2-Ethyl-5-undecyl-2-pyrroline       34153 000000-00-0 25

  7  21.60  4.14 C:\DATABASE\NBS75K.L
                 Sylvatesmin                         51542 000487-39-8 37
                 Cyclopropanenonanoic acid, 2-[(2-b  45907 010152-69-9 14
                 Benzene, 1-chloro-4-(methylsulfony  20164 000098-57-7 10

  8  21.63  7.27 C:\DATABASE\NBS75K.L
                 Cyclohexane, 1,1'-hexylidenebis-    34015 055030-20-1 35
                 Cyclohexane, (2,2-dimethylcyclopen  17943 061142-23-2 30
                 3-Octadecene, (E)-                  34414 007206-19-1 30
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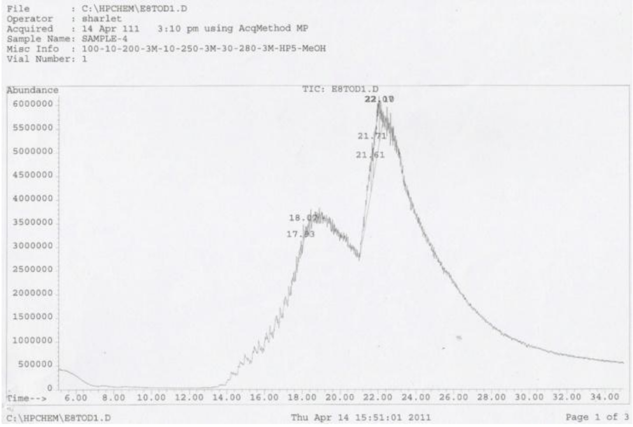

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Vial Number: 1
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C:\HPCHEM\E8TOD1.D              Thu Apr 14 15:51:01 2011              Page 1 of 3
```
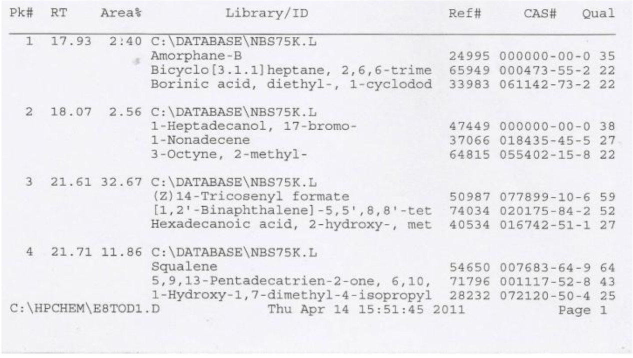

Fig.9. GCMS for catalyst Boric acid+MgO+KMnO$_4$

Compound formed for catalyst Boric acid+MgO+KMnO$_4$



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                 Amorphane-B                         24995 000000-00-0 35
                 Bicyclo[3.1.1]heptane, 2,6,6-trime  65949 000473-55-2 22
                 Borinic acid, diethyl-, 1-cyclodod  33983 061142-73-2 22

  2  18.07  2.56 C:\DATABASE\NBS75K.L
                 1-Heptadecanol, 17-bromo-           47449 000000-00-0 38
                 1-Nonadecene                        37066 018435-45-5 27
                 3-Octyne, 2-methyl-                 64815 055402-15-8 22

  3  21.61 32.67 C:\DATABASE\NBS75K.L
                 (Z)14-Tricosenyl formate            50987 077899-10-6 59
                 [1,2'-Binaphthalene]-5,5',8,8'-tet  74034 020175-84-2 52
                 Hexadecanoic acid, 2-hydroxy-, met  40534 016742-51-1 27

  4  21.71 11.86 C:\DATABASE\NBS75K.L
                 Squalene                            54650 007683-64-9 64
                 5,9,13-Pentadecatrien-2-one, 6,10,  71796 001117-52-8 43
                 1-Hydroxy-1,7-dimethyl-4-isopropyl  28232 072120-50-4 25
C:\HPCHEM\E8TOD1.D              Thu Apr 14 15:51:45 2011              Page 1
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