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Improvement of Fuel Quality by Oxidative Desulfurization: Design of Synthetic Catalyst for the Process

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Abstract

The present study explored a novel oxidative desulfurization (ODS) method of light gas oil fuel, which combines a catalytic oxidation step of the dibenzothiophene compound directly in the presence of molecular air as oxidant to obtain high quality fuel for light gas oil.

In chemical industries and industrial research, catalysis play a significant role. Heightened concerns for cleaner air together with stricter environmental legislations on sulphur content in addition to fulfill economic have created a driving force for the improvement of more efficient technologies and motivating an intensive research on new oxidative catalysts. As the lower quality fuel becomes more abundant, additional challenges arise such as more severe operation conditions leading to higher corrosion of the refinery installations, catalyst deactivation and poisoning. Therefore, among the technologies to face these challenges is to develop catalysts that can be applied economically under moderate conditions.

The objective of this work is to design a suitable synthetic catalyst for oxidative desulfurization (ODS) of light gas oil (LGO) containing model sulphur compound (dibenzothiophene (DBT)) using air as oxidant and operating under different but moderate operating conditions. The impregnation method is used to characterize two homemade catalysts, cobalt oxide (Co_3O_4/γ-Al_2O_3) and manganese oxide (MnO_2/γ-Al_2O_3). The prepared catalysts showed that the manganese oxide has a good impregnation (MnO_2=13%), good pore size distribution and larger surface area. A set of experiments related to ODS of dibenzothiophene has been carried out in a continuous flow isothermal trickle bed reactor using light gas oil as a feedstock utilizing both catalysts prepared in-house. At constant pressure of 2 bar and with different initial concentration of sulphur within dibenzothiophene, the temperature of the process was varied from 403K to 473K and the liquid hourly space velocity from(LHSV*)* was varied from 1 to 3 hr^{-1}. The results showed that an increase in reaction temperature and decreasing in LHSV, higher conversion was obtained.

Although both catalysts showed excellent catalytic performance on the removal of molecule sulphur compound from light gas oil, the catalyst MnO_2 catalyst exhibited higher conversion than Co_3O_4 catalyst at the same process operating conditions.

Key words

ODS, light gas oil, Trickle bed reactor, Cobalt oxide catalyst, Manganese oxide catalyst.

1. Introduction

Sulphur types (benzothiophene, dibenzothiophene and its derivatives) are the most notorious and undesirable petroleum contaminants and a large portion of those compounds can be transferred to diesel oil during refining of crude oil [1]. Major portions of the crude oils are used as transportation fuels such as gasoline, diesel and jet fuel. However, such crudes contain sulphur, typically in the form of organic sulphur compounds. Increasing the sulfur compounds lead to a significant impact upon the quality of crude oil in addition to the harm they can cause. The sulphur content and American Petroleum Institute (API) gravity are two main properties, which have a great influence upon the value of the crude oil [2].

A vast variety of sulphur compounds are present in light gas oil (LGO). These sulphur compounds can be classified into four main groups: mercaptans, sulfides, disulfides and thiophenes. Environmental concerns have driven the need to remove sulphur-containing compounds from LGO. Sulphur-containing compounds are of particular interest because of their tendencies to produce precursors to acid rain and airborne particulate material[3].

Oxidative desulfurization(ODS) process has been considered a promising method for deep desulfurization technology because it can be carried out under mild conditions (temperature and pressure), such as relatively low temperature, approach constant pressure and cost of operation when it is compared with hydrodesulfurization(HDS) process [4-7].

Various studies on the ODS process have used different oxidizing agents and catalysts, such as H_2O_2/acetic acid [8], ozone/heterogeneous catalysts [9], and O_2/aldehyde/cobalt catalysts [10]. The ODS process is usually carried out under mild conditions that present competitiveness over the conventional HDS process [11]. The oxidation of mercaptans present in different fuels is carried out in trickle bed reactors using air as oxidant, and UVKO-2 catalyst (commercial catalyst) and caustic as co-catalyst [12].

The deep desulphurization of fuel has drawn increasing attention due to new regulations and it is difficult or very costly to use hydrodesulphurization(HDS) process for reducing the sulphur in the fuels to less than 10 ppm. Also, depending on the feed and level of the desulfurization, the required operating conditions for HDS reactor are very high(573-723K and 35-270 bar) [11].

Most of the sulphur contamination in diesel can be traced to the dibenzothiophene derivatives. In order to remove these compounds by HDS, it would require more hydrogen capacity and maintenance of high temperature, pressure and high contact time. This would increase operating costs leading to enhanced likelihood that complete saturation of olefins and aromatics will occur resulting in losses of hydrocarbons. Thus, it is likely that HDS processing has reached a stage where increasing temperature and pressure are not economically justified to remove the residual sulphur without affecting the yield of diesel fuel from hydrotreatment processes[13]. Also, this process will increase the volume of hydrogen sulfide(H_2S). Although HDS processes have dominated desulphurization of petroleum in the past, their cost and the requirements of strict fuel specifications motivate to the development of innovative new technologies.

Oxidative desulphurization is based on the removal of heavy sulphides, usually in the form of polynuclear aromatics where one ring is a thiophene structure. In ODS, these compounds are oxidized by adding one or two oxygen atoms to the sulphur without breaking any carbon-sulphur bonds, yielding the sulfoxide and sulphones, respectively. These oxidized compounds can then be effectively extracted or adsorbed from downstream processing.

This work contributes to a growing understanding of light gas oil ODS. The oxidation by air of light gas oil using two catalysts (cobalt oxide ($Co_3O_4/\gamma\text{-}Al_2O_3$) and manganese oxide ($MnO_2/\gamma\text{-}Al_2O_3$)) prepared experimentally in-house, is studied to determine the extent of dibenzothiophene removal as well as to highlight operating issues that must be resolved in order to develop an industrially viable process.

2. Material used in Experimental Work with Catalysts Preparation

2.1 Materials Used

- Dibenzothiophene(DBT)

One type of model sulphur compound is selected to evaluate the reactivity of sulphur in an oxidation reaction. The dibenzothiophene (DBT) purchased from Aldrich Company with purity of 99%.

- Light Gas Oil (LGO)

The feedstock used in this study is the hydrotreated light gas oil (DBT concentration = 2 ppm, and sulphur content 7.8 ppm) that has been obtained from *North Refineries Company* in Iraq. The physical properties of feedstock illustrated in Table 1.

- Air

Air gas is used as oxidizing agent to oxidize sulphur compound to sulfoxide and sulphones.

2.2 Catalysts

Incipient Wetness Impregnation (IWI) method is a widely used method for catalyst design and characterization. It involves contacting a solid with a liquid containing the components to be deposited on the surface. The type of products depends on the nature of both reactants (the liquid and the solid surface) and the reaction conditions. In the Incipient Wetness Impregnation process (IWI), the active metal precursor with thermally unstable anions (nitrates, chloride, carbonates, and hydroxides) is used. Then the metal containing solution is added to a catalyst support having the same pore volume as the volume of solution that was added under precisely defined conditions (concentration, mixing, temperature, time) [14]. One of the best-known methods for producing catalysts is the impregnation of porous support materials with solutions of active components. Especially catalysts with expensive active components such as noble metals are employed as supported catalysts. After impregnation the catalyst particles are dried and calcinated to get rid of remained solvent and acquiring catalyst the physical and chemical properties[15].

Several chemical compounds are used for catalyst preparation:-

2.2.1 Active component

The active component used in preparation of the catalyst types are the cobalt nitrate ($Co(NO_3)_2.6H_2O$ with purity of 99.5%) using active component purchased from Alpha chemika Company, and the manganese acetate ($Mn(CH_3COO)_2.4H_2O$ with purity of 99%) using active component purchased from Sigma. Active component dissolved in deionized water that has been obtained from Samarra Company.

2.2.2 Support (Aluminum oxide (γ-Al_2O_3))

A commercial spherical shape aluminum oxide (γ-alumina) has been used as a carrier in manufacturing of the catalyst ,its specification is shown in Table 2.

2.3 Catalyst used in the Experimental Work

2.3.1. Preparation of Alumina Supported Cobalt Oxide and Alumina Supported Manganese Oxide:-

The prepared (CAT-1) cobalt oxide over gamma alumina catalyst (2% Co_3O_4/γ-Al_2O_3) is as following: the gamma alumina is put in the flask under condition of evacuation (using vacuum pump) in order to remove the gases out of the support pores, then the solution prepared is added to the gamma alumina at a rate of (15-20) drop per minute with continuous stirring where all the solution is impregnated (Figure

1). The temperature is kept constant at 373 K using bath water. Manganese oxide (CAT-2) is prepared by using same procedure (13%MnO_2/γ-Al_2O_3). The dried catalyst is calcinated for 5 hours in the oven at 823 K under laminar flow of air. The purpose of this step is that the most of the metal salts loaded on the γ-Al_2O_3 converted into their corresponding metal oxides leading to deposit of active metal oxide over the catalyst support in addition to acquiring the physical and chemical properties of the catalyst. Calcination step has been carried out in state company of *Fertilizer/Northern Area* - *Baiji*-Iraq[16]. Figure 2 shows the flow chart of preparation steps.

2.4 Oxidation Experiments in a Trickle Bed Reactor

2.4.1 Apparatus and Procedure

The experiments of this work were conducted at moderate temperature, moderate pressure trickle bed system in chemical engineering department/college of engineering/Tikrit University. Process flow diagram of this system is presented in Figure 3. The continuous oxidation process of LGO is carried out in a trickle bed reactor (TBR) with co-currently down-flow. The fixed bed reactor consists of a stainless steel 310 tubular reactor, 77 cm long, and 1.6 cm inner diameter and controlled automatically by four sections of 15 cm height steel-jacket heaters(Electrical coil). The LGO is stored in a feed tank, which is connected to a high-pressure dosing pump that can dispense flow rates from 0.0 to 1.65 litter/hr of LGO at pressure up to 20 bar. The oxidant gas (air gas) flows from a high-pressure air compressor equipped with pressure regulator to maintain constant operating pressure. Gas flow meter coupled with a high precision valve and control gas flow rate is used. The light gas oil (DBT concentration) and air gas streams are mixed before introduced to the reactor at the required temperature when dibenzothiophene are oxidized to sulphones. The outlet stream flows to a heat exchanger (shell and tube(sour tubes) stainless steel) at 293K then to high pressure gas-liquid separator in order to separate excess air from the treated LGO.

2.4.2 Experimental Procedure (Preparation of Trickle Bed Reactor)

2.4.2.1 Operation Conditions

In this work, various experiments were conducted with the following moderate operating conditions:-

- Initial concentration of DBT: 500, 800 and 1000 ppm.
- Temperature: 403, 443 and 473K.
- Liquid hour space velocity: 1, 2, and 3h^{-1}.
- Catalyst-types:CAT-1= $Co_3O_4/\gamma\text{-}Al_2O_3$ and CAT-2= $MnO_2/\gamma\text{-}Al_2O_3$.

2.4.2.2 Catalyst Loading

A complete catalyst bed is made up of three main parts; two parts of ceramic balls and a part of the catalyst is loaded in between them. The purpose of the diluents as well as the ceramic balls is to provide complete catalyst wetting and to reduce radial dispersion and the bed porosity leading to minimization of any diffusion effects and thus providing plug flow conditions for isothermal reactions. The optimal percent of inert layers (ceramic balls) in the catalyst bed is ranged to be between 30 to 35 % vol. [17]. In this work, the catalyst bed (58 cm^3) loaded with (40% $Co_3O_4/\gamma\text{-}Al_2O_3$) between two layers of (30% ceramic balls) is considered (as shown in Figure 4 ~~5~~).

2.4.3 Running of Experiments

After loading the catalyst inside the reactor and securing the lower and upper flanges carefully, the following steps are performed to prepare and run the experiments:-

- Flow the air gas through the reactor at 2-bar pressure.

- Set the temperature controller to the feed injection temperature (it is lower than steady state operating temperature), then temperature raise with the rate 293 K per hour.
- Turn on of dosing pump at a certain of light gas oil flow rate when temperature of air reaches feed injection temperature.
- Raise the temperature at rate of 293K per hour until reach steady state temperature.
- When the system reaches steady state condition, samples are collected.
- Turn off light gas oil dosing pump and keeping air gas flowing to back wash of remains light gas oil, then close air valve and allow the nitrogen to flow inside the system to remove air.

2.4.4 DBT Analysis (GC-capillary Chromatography)

Dibenzothiophene content in feedstock and product are analyzed according to GC-capillary chromatography. These are as follows:

- Colum : CP-Sil 8 CB fused silica WCOT
  30 m x 0.25 mm , df = 0.25 μm
  Cat. No. CP8751
- Temperature : 313K(2 min) → 553K, 283K/min
- Carrier gas : He, 39 cm/s, 128 KPa (1.28 bar, 18.6 psi)
- Injector : Splitless,
  : T = 523K
- Detector : FID,
  : T = 573K
- Sample size : 2 μm
- Concentration range : 10 ppm

The determination of the outlet concentration of dibenzothiophene unreacted can be accomplished by reading the value from the computer.

2.5 Characterization of the Catalyst Prepared

2.5.1 Activity

After preparing the catalyst, its performance should be checked and its reliability towards oxidation of dibenzothiophene as well. These issues were performed in a lab scale apparatus. Throughout the catalyst development, activity is a key parameter in design, selection and optimization. Comparison was made between the homemade prepared catalysts (CAT-1=$Co_3O_4/\gamma\text{-}Al_2O_3$) and (CAT-2=$MnO_2/\gamma\text{-}Al_2O_3$).

2.5.2 Bulk Density (Packing Density)

Bulk density is the ratio of the weight of the catalyst particle to the bed volume occupied by the catalyst particle. This property was determined by randomly placing 50 cm^3 of dried catalyst in the cylinder. The weight difference between the cylinder filled with catalyst (namely, W_2) and the empty on (namely as, W_1), represents the catalyst weight therefore, bulk density is determined as follows:

$$\rho_B = \frac{W_2 - W_1}{V} \qquad \text{………………………………...……………………...………(1)}$$

2.5.3 Pore Volume

A direct simple method for determining the total volume of pores is by measuring the increase in weight when pores are filled with liquid. This should preferably be of low molecular weight so that fine pores are filled (e.g. water or various hydrocarbons may be used). A general procedure is the liquid impregnation method[18]. This is commenced when a sample of dry catalyst of known weight (W_3) is immersed in boiled water. The entire sample should then be transferred to a damp cloth, rolled to remove excess water and weighted (W_4). Hence, the total pores volume was calculated as follows:-

$$V_P = \frac{W_4 - W_3}{W_3\ \rho_B} \qquad \text{……………………………………………..……..…(2)}$$

Table 6 showed the characteristic of the prepared catalysts.

Regarding to this Table, it can be seen that after impregnation with active component, the surface area and pore volume are reduced significantly for different catalysts because the active component occupies some space and increases the bulk density of the samples.

3. Results and Discussions

3.1 Effect of Operating Variables on the Oxidation Processes

The experimental runs were carried out in a trickle bed reactor using cobalt oxide and manganese oxide as catalyst. The effects of catalysts type, LHSV, temperature, and dibenzothiophene concentrations are discussed here.

3.1.1 Determination of the Most Active Catalyst and the Optimum Condition

Figure 5 and 6 presents a comparison of the activities of the prepared catalysts. Both catalysts showed similar behavior. The differences between the catalysts can be attributed to their differences in physical and/or chemical properties. Regarding the results of using CAT-1. and CAT-2. it seems that the activity of these catalysts is related to the metal dispersion, BET surface area, porosity, and bulk density. Based on the results presented in these Figures, the catalysts can be ranked as follows in terms of activity in dibenzothiophene oxidation.

CAT-2 > *CAT*-1

Also, it is clearly observed that the best conversion is obtained at the following operating conditions:-

- The best temperature is (473K).
- The best *LHSV* is 1 hr^{-1}.
- The initial concentration of dibenzothiophene of (1000 ppm).
- The best catalyst is CAT-2.

The effects of metal loading and reaction temperature were investigated in this process. Where, below 403K, the oxidation reaction was not observed and there was a significant difference in conversions for the oxidation of model diesel for catalyzed by either CAT-2 and 403, 443, 473K at 1, 2, 3 hr^{-1} and high conversion from CAT-1is found.

3.1.2 Effect of Temperature on the Process Conversion

For the influence of temperature upon the conversion of dibenzothiophene oxidation to sulphone, the experimental data are tabulated in Tables 4-9.

Figure 7 shows that at 1 hr^{-1} and 473K, dibenzothiophene conversion is 81.2%, while at 443K and 403K, dibenzothiophene conversions are 53.4 % and 32.7 % respectively for CAT-2. The general behavior is, higher conversion is achieved at higher temperature due to the fact that at high temperature, kinetic constant (reaction rate constant) is favorably affected resulting in increasing in dibenzothiophene conversion[16]. The maximum conversion obtained in this study compared with higher conversion reported in the literature can be attributed to the moderate operating conditions (for safety purposes) used here in addition to the use of air as oxidant (for economic issues) containing oxidant percentage of 21% leading to incomplete conversion (100%).

Also, increasing in temperature will contribute to an increase of magnitudes of some important physical properties such as Henry's constant and diffusivity, and decreasing of viscosity and surface tension. However, the increase in temperature levels will raise the absorption rate of molecular air in liquid and the diffusion rate of dibenzothiophene and the rate of dissolved air inside catalyst pores, which reach the active sites when oxidation reaction occurs[19], as show in Figure 7 and 8.

3.1.3 Influence of Liquid Hour Space Velocity

The effect of *LHSV* on dibenzothiophene removal rate is shown in Tables 4-9. As can be seen, increasing *LHSV* has an adverse impact on dibenzothiophene conversion, Figure 9 and 10 depicts the effect of liquid flow rate on dibenzothiophene conversion. As clearly noted from Figure 10, dibenzothiophene conversion at 473K of 81.2% is achieved at *LHSV*=1 hr^{-1}. At *LHSV* of 2 and 3 hr^{-1}, dibenzothiophene conversion were 60.9% and 51.1% respectively. Actually, increasing liquid flow rate reduces the residence time of the reactant thus reducing the time of reaction of dibenzothiophene with air (gas reactant). Moreover, higher liquid flow rates give greater liquid holdup, which evidently decrease the contact of liquid and gas reactants at the catalyst active site, by increasing film thickness. The results reported in the literature were confirm such behavior [20,21].

3.1.4 Impact of Initial Dibenzothiophene Concentration

The influence of initial concentration of dibenzothiophene is studied at 500 ppm, 800 ppm, and 1000 ppm. In the range of these experiments, dibenzothiophene conversion decreases by decreasing inlet dibenzothiophene concentration as illustrated in Figure

11. It has also been noticed that dibenzothiophene conversion decreases from 78 to 69.2% at 1 hr^{-1} for CAT-1, when dibenzothiophene concentration decreases from 1000 to 500 ppm. This can be attributed to the fact that decrease dibenzothiophene molecules coverage the active site over the catalyst surface and/or proves that catalyst deactivation take place. This also suggested that when the reaction is carried out with proper air and dibenzothiophene loads oxides, catalyst deactivation can be avoided[22].

Figure 11 and 12 and Tables 4-9 mentioned previously showed that the conversion has been affected by the initial concentration of dibenzothiophene(direct proportion), but the change in the conversion by changing the initial concentration of dibenzothiophene was approximately little compared with CAT-1. This is due to high active metal (manganese oxide) toward dibenzothiophene oxidation beside alumina supported from cobalt oxide, which characterizes as a good adsorbent for dibenzothiophene. Hence, the catalyst CAT-2 has high capability of adsorption/oxidation dibenzothiophene species at high and low initial dibenzothiophene concentration. It is also observed that dibenzothiophene conversion decreases from 81.2 to 73.5% at 1 hr^{-1} for CAT-2, when dibenzothiophene concentration decreases from 1000 to 500 ppm.

3.2 Influence of Oxidation Process on Physical Properties of Feedstock

The physical properties and ASTM distillation of feedstock and product at optimum operating condition (CAT-2, temperature = 473K, $LHSV$=1 hr^{-1}, dibenzothiophene initial concentration=1000 ppm) is shown in Table 10 and plotted in Figure 13.

Generally, it is obvious from Table 10 and Figure 13 that there is no high difference in physical properties and ASTM distillation between feedstock and product at the optimum operating condition. This attributes to the following reasons:-

- Density, viscosity, and boiling range are approximately the same before and after oxidation reaction because there was no high change in the components of the hydrotreated light gas oil.
- Reid vapor pressure (RVP) decrease slightly due to reaction of some of the volatile compounds.
- Aniline points (AN) and research octane number (RON) are approximately same before and after oxidation reaction due to the aromatic compounds not being involved in the oxidation reaction, so that they are not broken or saturated as in hydrodesulphurization process.

4. Conclusions

This study aimed at designing a suitable synthetic catalyst which can be applied to an oxidative desulphurization (ODS) of light gas oil. The impregnation method is used to characterize two homemade catalysts: cobalt oxide ($Co_3O_4/\gamma\text{-}Al_2O_3$) and manganese oxide ($MnO_2/\gamma\text{-}Al_2O_3$). Using both catalysts, a set of experiments related to ODS process have been carried out in a continuous flow isothermal trickle bed reactor using light gas oil as a feedstock and air as oxidant under different operating conditions. The following observations are made from this study:-

- The two catalyst classes studied here is found to be more selective ($Co_3O_4/\gamma\text{-}Al_2O_3$ and $MnO_2/\gamma\text{-}Al_2O_3$) to the oxidation reaction of dibenzothiophene based on the experimental results.
- Among the two catalysts, the manganese oxide showed a good impregnation (MnO_2=13%), compared to cobalt oxide (2% CO_3O_4). Although the catalytic

performance of both catalysts in terms of the removal of sulphur compound from, the catalyst MnO_2 catalyst outperforms Co_3O_4 catalyst at the same process operating conditions.

- The most difficult sulphur products to be removed by hydrotreatment in diesel, can be fully oxidized using an air as oxidant and cobalt oxide and manganese oxide materials as catalysts in the absence of any solvent.
- The achievement of very low levels of sulphur required in transportation fuels in the near future which will be difficult and/or will be highly costly by current hydrodesulphurization process (HDS). Several alternative strategies to HDS process are currently being explored, amongst them is the oxidative desulphurization techniques (ODS) that do not require the use of expensive hydrogen.
- Yields of oxidation reaction is normally affected very much by severity of increasing in operation conditions such as (temperature, liquid hour space velocity and initial concentration) as well as the type of the catalyst used.
- The oxidative desulfurization process has two advantages compared with other reported oxidative desulfurization processes. The first one is that the reaction can be carried out at middle temperature and within a very short reaction time. The second is that air can be used as an efficient oxidant compared to costly oxidants, such as H_2O_2, ozone and TBHP, which were reported in the literatures for the oxidative desulfurization processes.
- It has also been observed that temperature is the most important factor effecting on the oxidation reactions. Liquid hourly space velocity (*LHSV*) has also a significant impact on the oxidation reactions owing to the effect of

contact time between feed and catalyst. As well as, active component has an important influence upon the oxidation reaction.

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Table Captions

Table 1: Properties of light gas oil (LGO).

Table 2: Aluminum oxide (γ-Al_2O_3) specification.

Table 3: The characteristic of the prepared catalysts.

Table 4: Experimental results obtained for CAT-1at (Initial dibenzothiophene concentration CA = 1000 ppm).

Table 5: Experimental results obtained for CAT-1 at (Initial dibenzothiophene concentration CB = 800 ppm).

Table 6: Experimental results obtained for CAT-1 at (Initial dibenzothiophene concentration CC=500 ppm).

Table 7: Experimental results obtained for CAT-2 at (Initial dibenzothiophene concentration CA = 1000 ppm).

Table 8: Experimental results obtained for CAT-2 at (Initial Dibenzothiophene concentration CB = 800 ppm).

Table 9: Experimental results obtained for CAT-2 at (Initial dibenzothiophene concentration CC=500 ppm).

Table 10: Physical properties of feedstock (light gas oil) before and after oxidation process

Figure Captions

Figure 1: Catalyst preparation apparatus.

Figure 2: Flow chart of preparation steps.

Figure 3: Process flow diagram of trickle bed reactor.

Figure 4: Schematic diagram of the catalyst loading in the reactor.

Figure 5: Comparison of the activities of the catalysts. Reaction conditions (Concentration of dibenzothiophene 1000 ppm, and T=473 K).

Figure 6: Comparison of the activities of the catalysts. Reaction conditions (Concentration of dibenzothiophene 500 ppm, and LHSV =1hr-1).

Figure 7: Effect of temperature on oxidation process of dibenzothiophene conversion (CAT-2, initial dibenzothiophene concentration = 1000 ppm).

Figure 8: Effect of temperature on oxidation process of dibenzothiophene conversion (CAT-1, initial dibenzothiophene concentration= 800 ppm).

Figure 9: Effect of temperature on oxidation process of dibenzothiophene conversion (CAT-1, dibenzothiophene concentration =1000 ppm).

Figure 10: Effect of LHSV on oxidation process of dibenzothiophene conversion (CAT-2, dibenzothiophene concentration =1000 ppm).

Figure 11: Effect of initial concentration on oxidation process of dibenzothiophene conversion (CAT-1, LHSV=1 hr-1).

Figure 12: Effect of *LHSV* on oxidation process of dibenzothiophene Conversion (CAT-2, at 443K).

Figure 13: ASTM of light gas oil treated before oxidation and after oxidation process.

Table 1: Properties of light gas oil (LGO).

Physical property	**LGO**
Specific gravity	0.851
Viscosity (cSt) at (293K)	4.9
Flash point,(^oC)	55
Total sulphur, (ppm)	9.8
Cetane index	52
Colour	0.5
Pour point,(^oC)	-39
API gravity	34.8

Table 2: Aluminum oxide (γ-Al_2O_3) specification.

Catalyst	**γ-Al_2O_3**
Pore volume, (cm^3/g)	0.5367
Bulk density,(g/cm^3)	0.671
Surface area, (m^2/g)	289
Particle diameter, (mm)	1.6
Particle shape	Sphere

Table 3: The characteristic of the prepared catalysts.

Catalyst issues	**γ-Al_2O_3**	**Co_3O_4/γ-Al_2O_3**	**MnO_2/γ-Al_2O_3**
Active phase $Co(NO_3)_2.6H_2O$%	-	2	-
Active phase Mn $(CH_3COO)_2.4H_2O$, %	-	-	13
Support	-	γ-Al_2O_3	γ-Al_2O_3
Calcinations temperature, K	-	823	823
Pore volume ($\boldsymbol{V_g}$), cm^3/g	0.5367	0.5021	0.476
Bulk density ($\boldsymbol{\rho_B}$), g/cm^3	0.671	0.692	0.7188
Surface area ($\boldsymbol{S_g}$), m^2/g	289	250	212
Particle diameter ($\boldsymbol{d_p}$), mm	1.6	1.6	1.6
Particle shape	Sphere	Sphere	Sphere

Table 4: Experimental results obtained for CAT-1 at (Initial dibenzothiophene concentration CA = 1000 ppm).

Temperature (K)	**LHSV (hr^{-1})**	**DBT concentration (ppm)**	**DBT conversion**
403	1	701.760	0.298
403	2	760.230	0.240
403	3	877.190	0.123
443	1	460.640	0.539
443	2	614.968	0.385
443	3	722.470	0.278
473	1	220.000	0.780
473	2	408.000	0.592
473	3	501.790	0.498

Table 5: Experimental results obtained for CAT-1 at (Initial dibenzothiophene concentration CB = 800 ppm).

Temperature (K)	**LHSV (hr^{-1})**	**DBT concentration (ppm)**	**DBT conversion**
403	1	586.809	0.267
403	2	634.657	0.207
403	3	717.110	0.104
443	1	410.598	0.487
443	2	510.600	0.362
443	3	635.286	0.209
473	1	199.546	0.751
473	2	352.270	0.559
473	3	450.436	0.437

Table 6: Experimental results obtained for CAT-1 at (Initial dibenzothiophene concentration CC=500 ppm).

Temperature (K)	LHSV (hr^{-1})	DBT concentration (ppm)	DBT conversion
403	1	379.577	0.241
403	2	407.661	0.185
403	3	458.840	0.082
443	1	272.823	0.454
443	2	342.989	0.314
443	3	414.986	0.170
473	1	153.926	0.692
473	2	236.946	0.526
473	3	289.723	0.421

Table 7: Experimental results obtained for CAT-2 at (Initial dibenzothiophene concentration CA = 1000 ppm).

Temperature (K)	**LHSV (hr^{-1})**	**DBT concentration (ppm)**	**DBT conversion**
403	1	672.653	0.327
403	2	748.324	0.252
403	3	850.625	0.149
443	1	465.768	0.534
443	2	624.368	0.376
443	3	715.296	0.285
473	1	188.123	0.812
473	2	390.826	0.609
473	3	488.758	0.511

Table 8: Experimental results obtained for CAT-2 at (Initial dibenzothiophene concentration CB = 800 ppm).

Temperature (K)	**LHSV (hr^{-1})**	**DBT concentration (ppm)**	**DBT conversion**
403	1	560.267	0.299
403	2	620.625	0.224
403	3	706.357	0.117
443	1	392.985	0.509
443	2	512.303	0.360
443	3	629.267	0.213
473	1	175.278	0.781
473	2	329.986	0.588
473	3	435.463	0.456

Table 9: Experimental results obtained for CAT-2 at (Initial dibenzothiophene concentration CC=500 ppm).

Temperature (K)	**LHSV (hr^{-1})**	**DBT concentration (ppm)**	**DBT conversion**
403	1	359.672	0.281
403	2	392.762	0.214
403	3	448.652	0.103
443	1	260.268	0.479
443	2	339.869	0.320
443	3	408.687	0.183
473	1	132.532	0.735
473	2	217.472	0.565
473	3	271.989	0.456

Table 10: Physical properties of feedstock (light gas oil) before and after oxidation process

Specification	**LGO Before ODS**	**LGO After ODS**
RVP psig (312 K)	16.3	15.8
Viscosity cst (293 K)	4.9	4.7
Density (gm/cm3)	0.851	0.8423
°API	34.8	36.4
AP (K)	412	416
RON	83	87

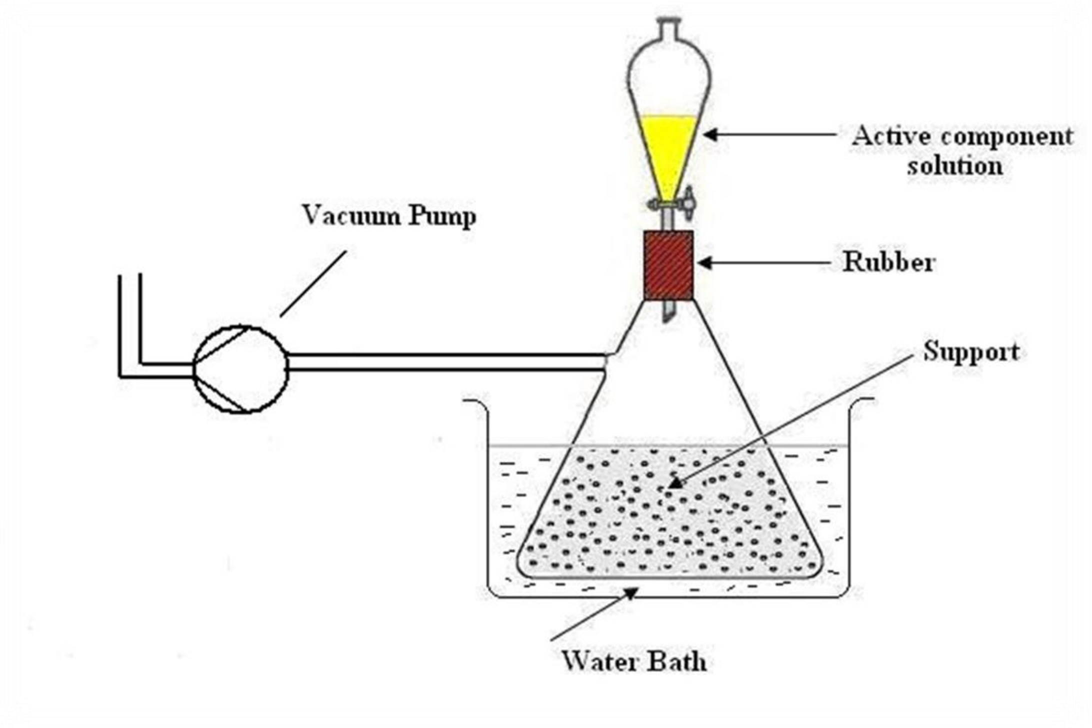
Active component solution
Vacuum Pump
Rubber
Support
Water Bath

Figure 1

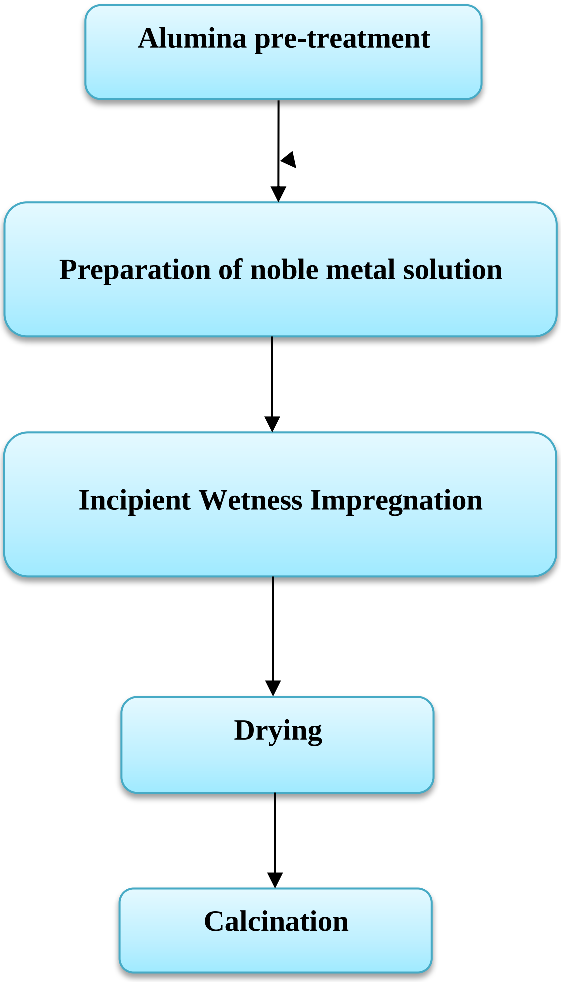
Alumina pre-treatment
Preparation of noble metal solution
Incipient Wetness Impregnation
Drying
Calcination

Figure 2

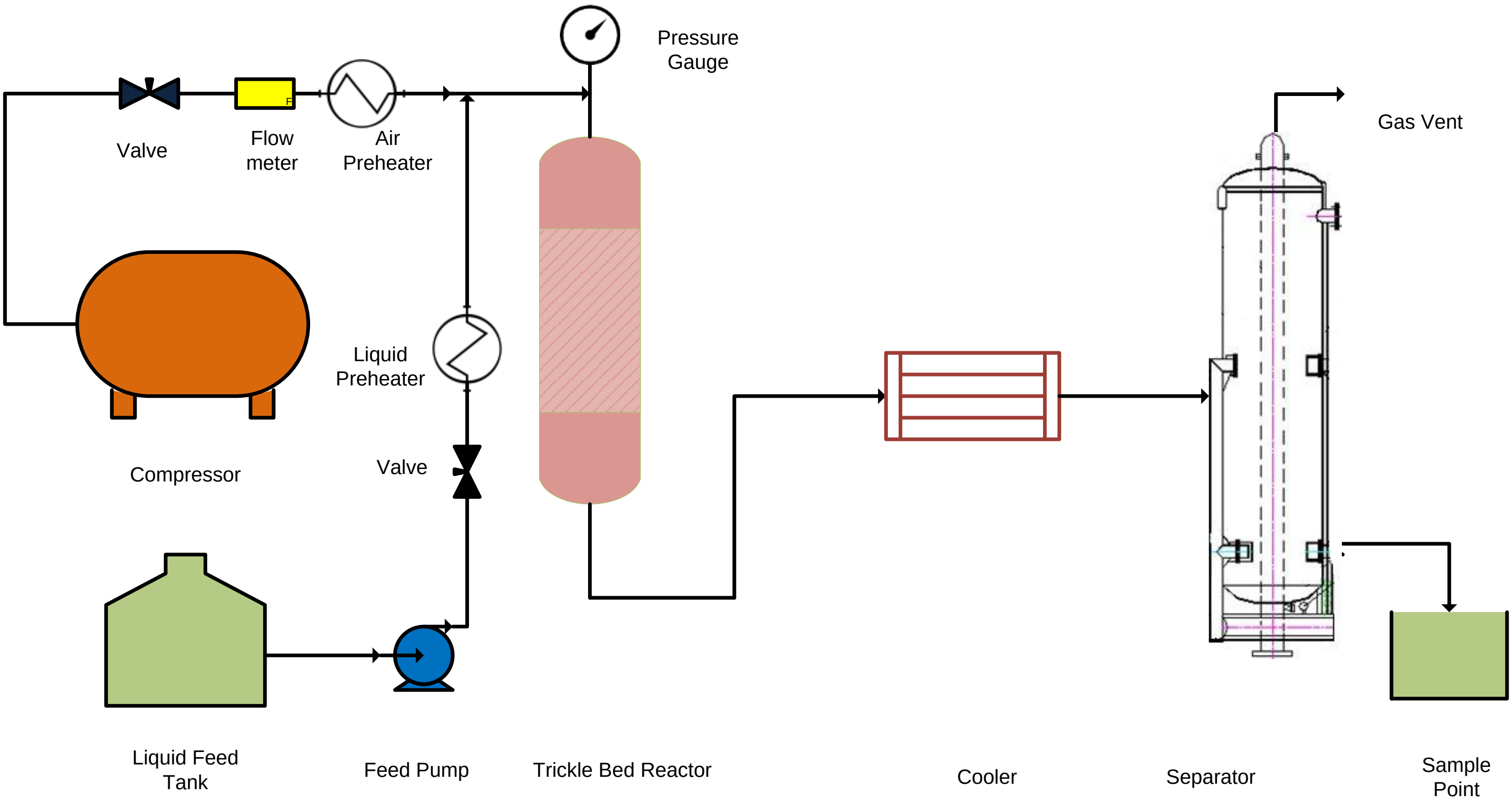
Pressure Gauge
Gas Vent
Valve
Flow meter
Air Preheater
Liquid Preheater
Compressor
Valve
Liquid Feed Tank
Feed Pump
Trickle Bed Reactor
Cooler
Separator
Sample Point

Figure 3

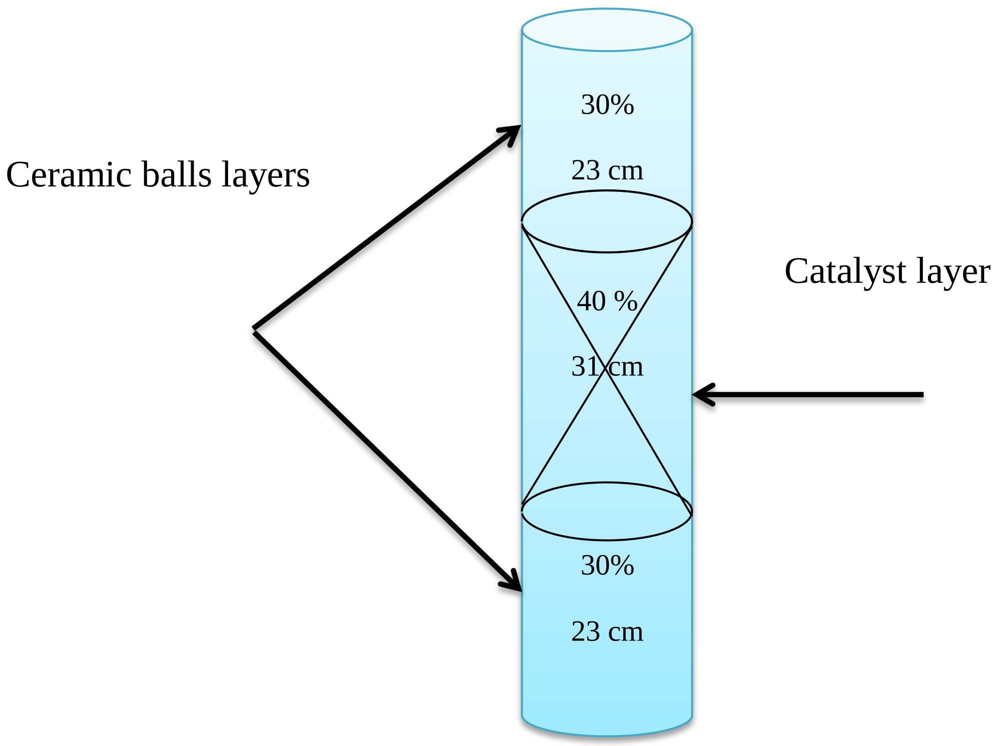

Figure 4

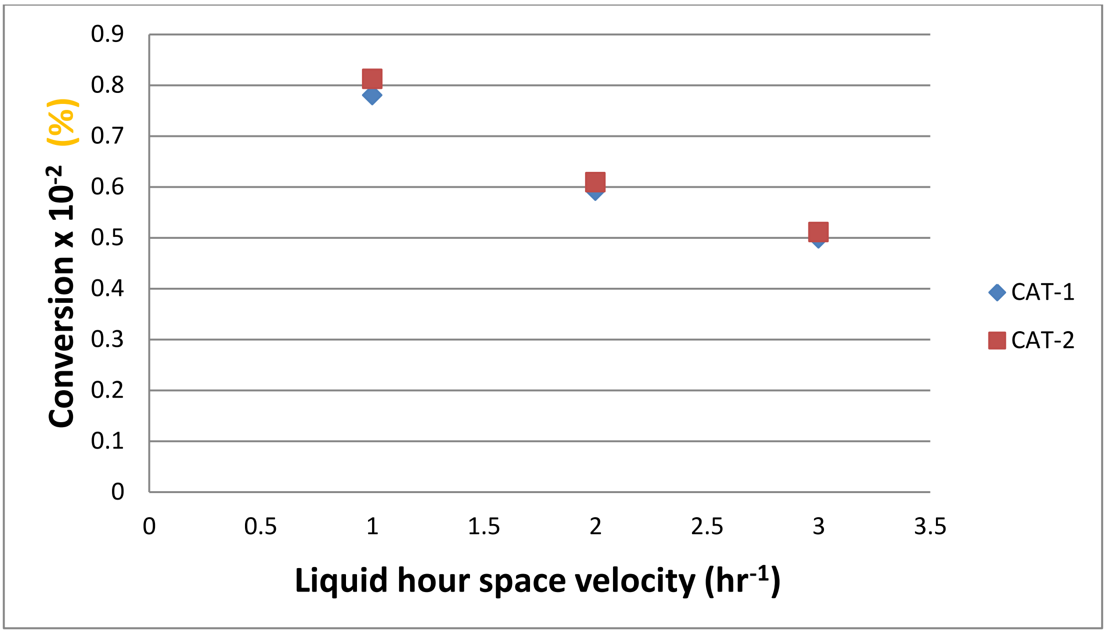
Conversion x 10-2 (%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
3.5
Liquid hour space velocity (hr-1)
CAT-1
CAT-2

Figure 5

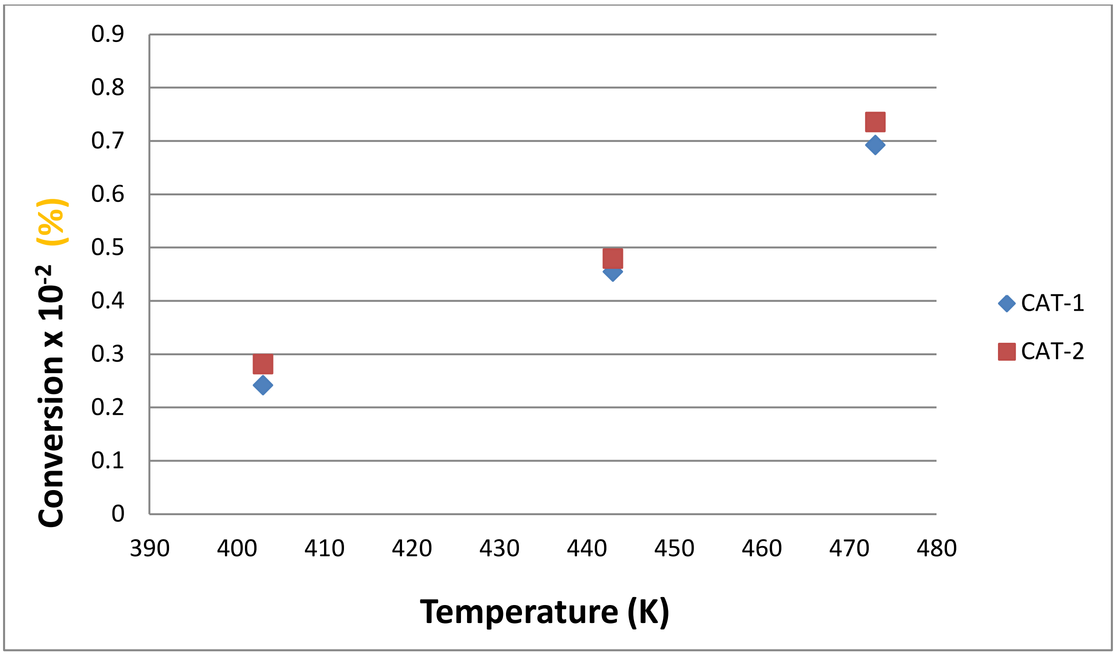
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Conversion x 10-2 (%)
390
400
410
420
430
440
450
460
470
480
Temperature (K)
CAT-1
CAT-2

Figure 6

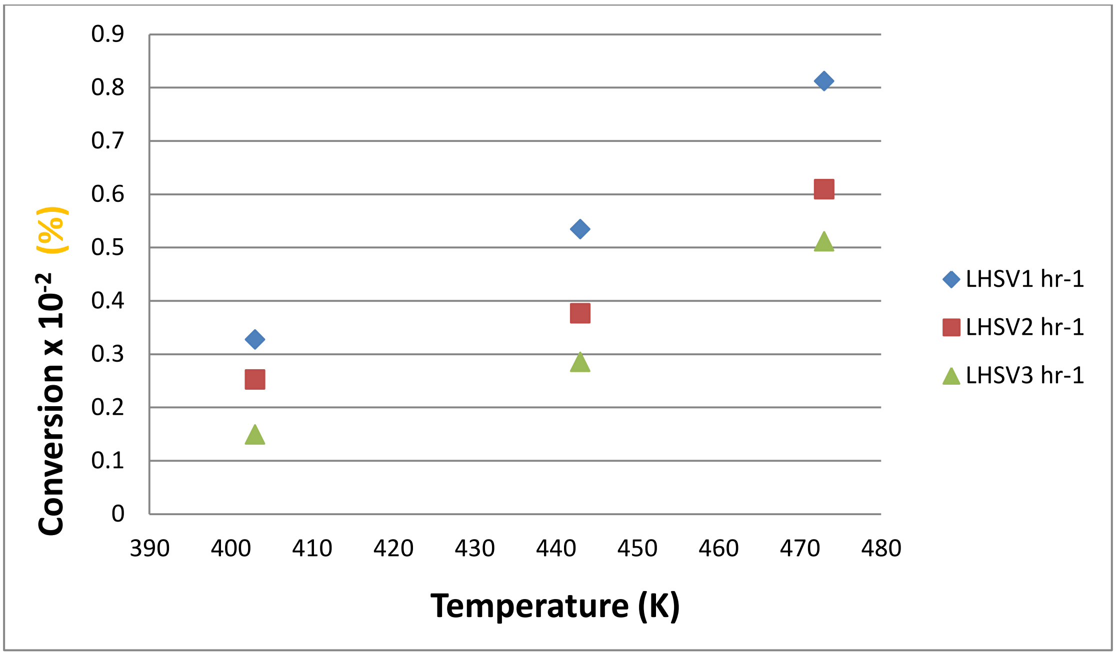
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
390
400
410
420
430
440
450
460
470
480
Temperature (K)
Conversion x 10-2 (%)
LHSV1 hr-1
LHSV2 hr-1
LHSV3 hr-1

Figure 7

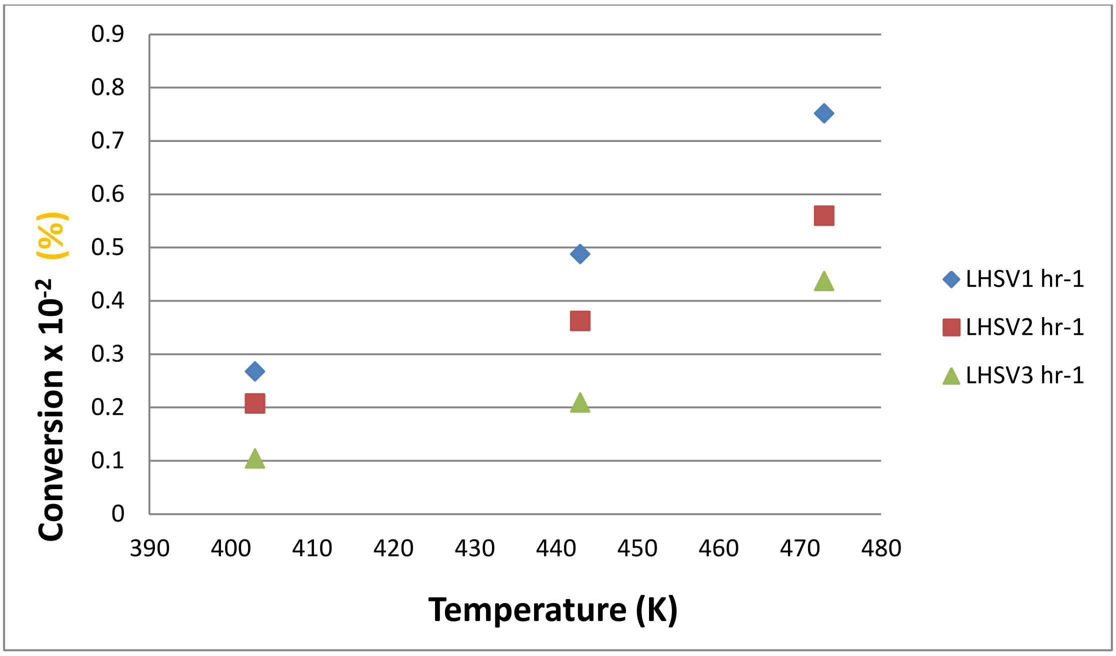
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Conversion x 10-2 (%)
390
400
410
420
430
440
450
460
470
480
Temperature (K)
LHSV1 hr-1
LHSV2 hr-1
LHSV3 hr-1

Figure 8

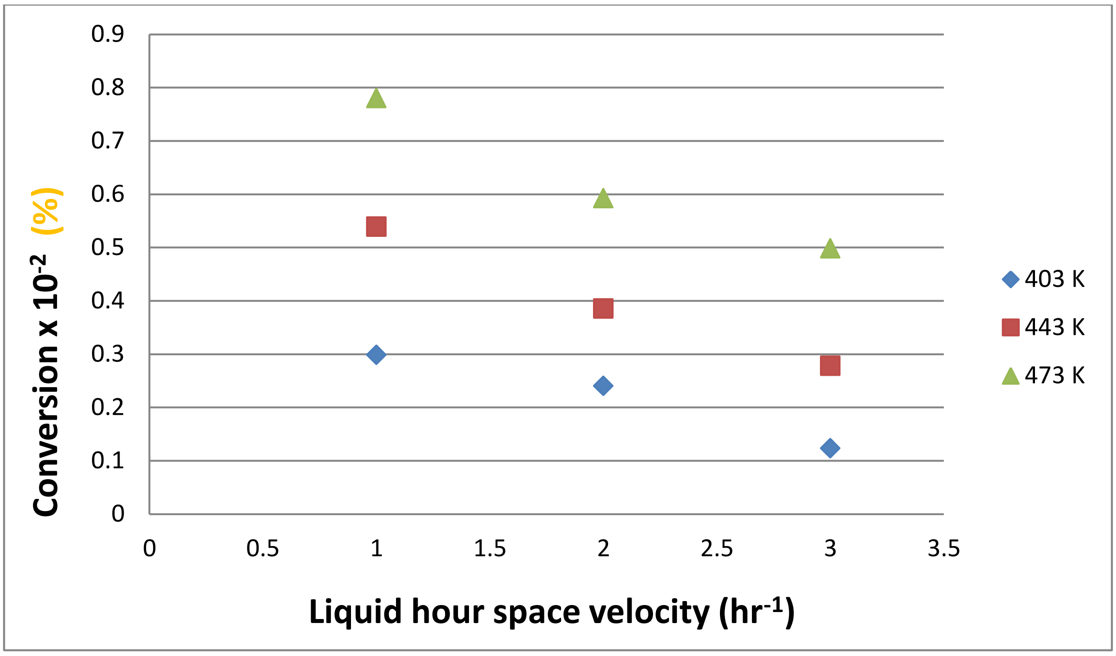
Conversion x 10-2 (%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
3.5
Liquid hour space velocity (hr-1)
◆ 403 K
■ 443 K
▲ 473 K

Figure 9

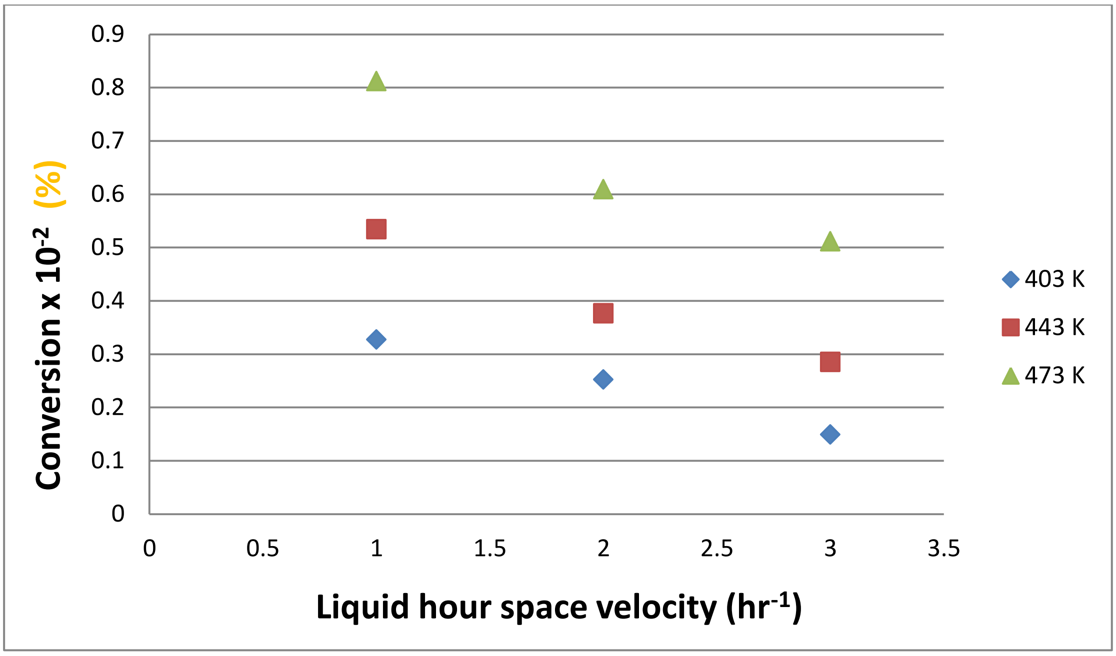
Conversion x 10-2 (%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
3.5
Liquid hour space velocity (hr-1)
403 K
443 K
473 K

Figure 10

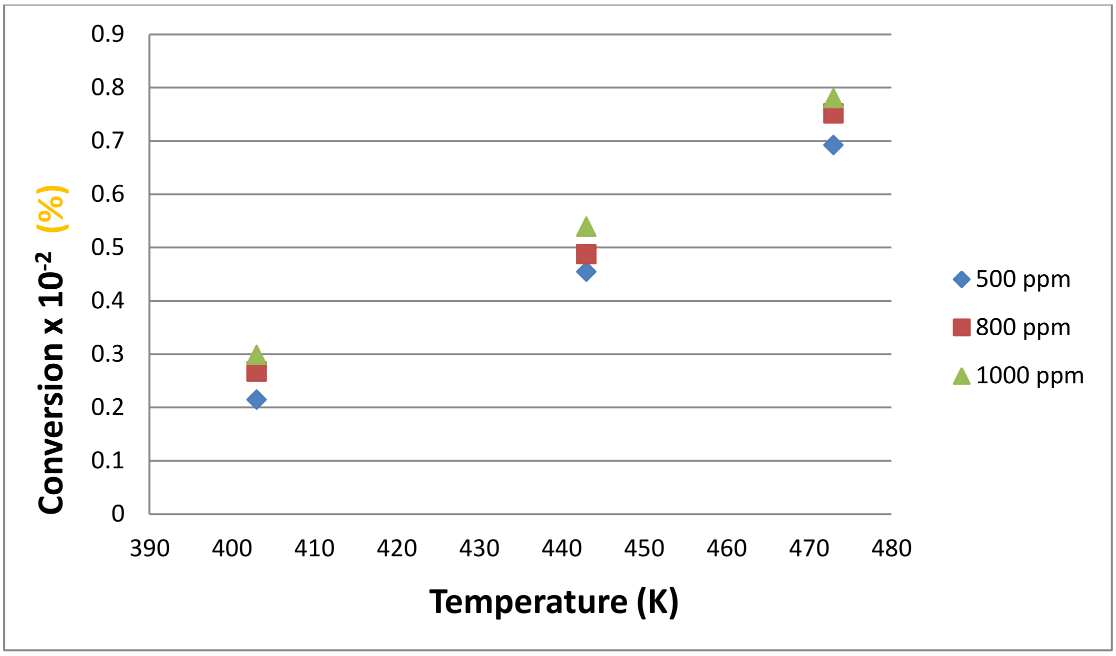
Conversion x 10-2 (%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
390
400
410
420
430
440
450
460
470
480
Temperature (K)
500 ppm
800 ppm
1000 ppm

Figure 11

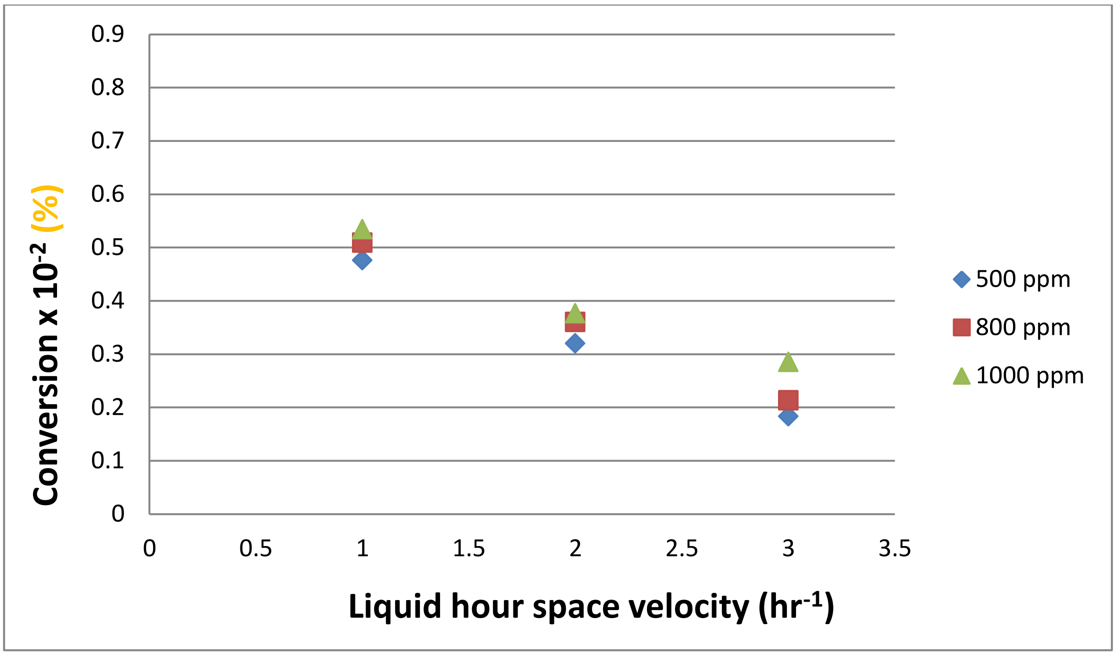
Conversion x 10-2 (%)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.5
1
1.5
2
2.5
3
3.5
Liquid hour space velocity (hr-1)
500 ppm
800 ppm
1000 ppm

Figure 12

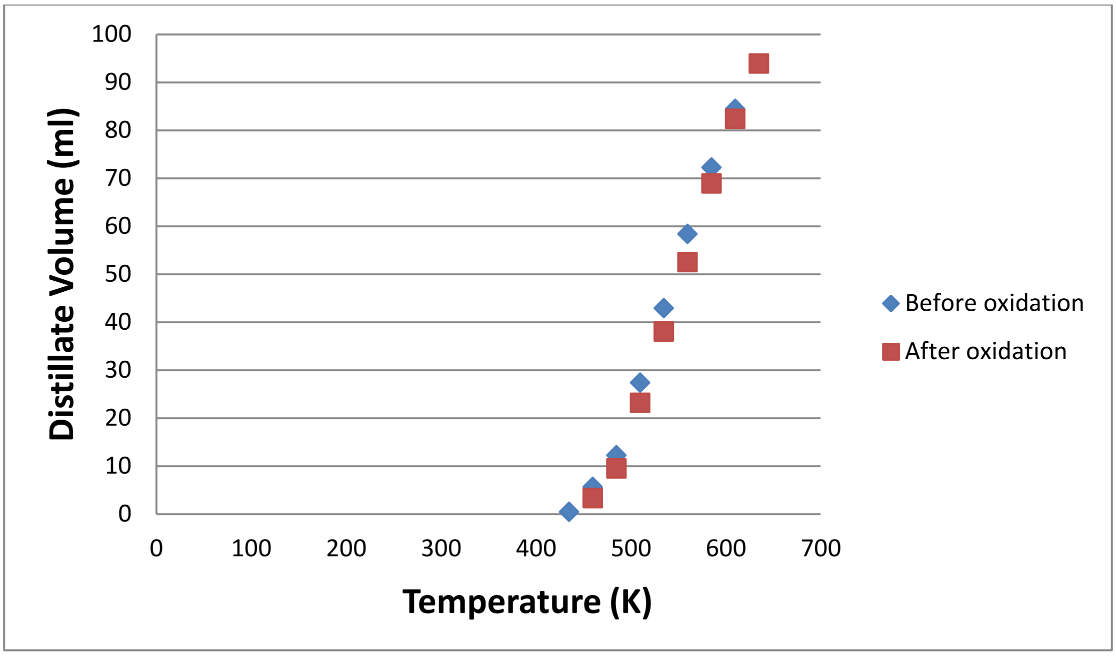
Distillate Volume (ml)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
Temperature (K)
◆ Before oxidation
■ After oxidation

Figure 13