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Life Cycle Analysis Based Evaluation of Desulfurisation Technologies

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Abstract

The study evaluates current desulfurisation technologies, namely hydrodesulfurisation (HDS), oxidativedesulfurisation (ODS) and supercritical fluid methods (SCF) considering different stages of life cycle. To evaluate these technologies, a functional unit of mass per unit of weight was chosen to weigh the environmental damage caused by each process. The assessment criteria include energy consumption categories (electricity, fuel oil, and diesel) and environmental impacts categories (global warming, acidification, and photochemical ozone formation). The total environmental impact was calculated based on Eco-99 indicators. Of the total environmental impacts, production is the most critical for both HDS and ODS technologies. Overall, SCF is identified as most energy saving technique. The influence of three processes on the environmental performance and the desulfurisation efficiency is studied using experimental design method. The use of this method helps to see how the process parameters interact. Statistical analysis showed that the most significant influence among different steps in these processes is the extraction of sulphur. This has opened upon opportunity to consider novel extraction method to minimize environmental impact.

Keywords: desulfurization; environmental assessment; mathematical model; supercritical fluid; life cycle analysis; indicators.

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1. Introduction

The extraction method based on the solubility of sulphur contents in appropriate solvent. The production of diesel creates large quantities of emissions due to impurities in the crude oil. Sulfur compounds are one of the major impurities in diesel that have a critical effect on the environment (e.g. global warming, acidification, and photochemical ozone formation) due to the sulfur. Although sulfur compounds production has become a critical issue worldwide, their toxic effects have led to alternative methods. Thus, the environmentally adverse impacts of sulfur emissions motivated scientists and engineers to look for alternatives such as hydrodesulfurisation and oxidative desulfurization techniques. These techniques have been tested and upgraded in recent years; however, still 6-8% of sulfur remains unrecovered. Table 1 shows the percentages of sulfur among Non-Organization of Petroleum Exporting Countries (OPEC) and Organization of Petroleum Exporting Countries OPEC. These fluctuations demonstrate the technical and theoretical gap between the two groups. In the past decades, although desulfurization techniques have made noticeable progress in efficiency, it necessitates some extra desulfurization capacity. Thus, various desulfurization processes have been developed for meeting requirements of increasingly stringent air emission regulations based on the level of sulphur content [4, 5]. Furthermore, improving both operational and environmental quality of diesel production can be achieved by reducing sulfur efficiently. This study introduces the use of supercritical carbon dioxide (scCO₂) which has properties of liquid and gas properties at a critical state, which create unique properties by increasing the mass transfer and improving the diffusivity of sulfur compounds. Application of supercritical carbon dioxide (scCO₂) is reviewed in this study due to its excellent properties (T=31.1 °C and P=73.1 bar). It is also non-flammable; non-toxic has a low critical temperature, and is cheap. Hydrodesulfurisation (HDS) is used to remove sulfur compounds from petroleum products such as light, medium, and heavy oil. The main purpose of extracting sulfur is to reduce the resulting sulfur emission from oil products as diesel. The goal of the HDS method is to treat sulfur by using hydrogen and form hydrogen sulfur (H₂S). However, the conventional HDS method cannot achieve very low sulfur reduction (>500ppm). More expensive catalysts are required to produce ultralow sulfur diesel (>15ppm). The cost of HDS, due to its high-energy demands, requirement of H₂ and low efficiency for cyclic compounds, extraction has led to initiatives for alternative desulfurization process. The oxidative technique (ODS) is described in Figure 1. It consists of two steps; the oxidation process and a sulfur reaction step. In the oxidation step, appropriate oxidant is supplied which converts sulfur compounds to sulfone compounds. The extraction of sulfur takes place by removing the sulfone compounds from the mixture which is then used for further applications.

It is obvious from previous studies that conventional solvents and ionic liquids are miscible with oil and are very expensive. However, supercritical carbon dioxide (scCO₂) is significantly miscible with oil and is also less costly than conventional solvents. Thus, scCO₂ can be used to enhance the reaction rate and maximize the converted fractionated oil. Although scCO₂ is widely used, it has the disadvantage of low solubility of the polar compounds. However, adding small amount of co-solvent can solve this hurdle. Then modified SCF with the co-solvent can increase the solubility and improve the physical interaction between solute and solvent. A review of the research and the development of desulfurization techniques are the goals of the study. Also, life cycle analysis (LCA) for comparative purposes is applied to determine the great impact of these techniques, using eco-99.

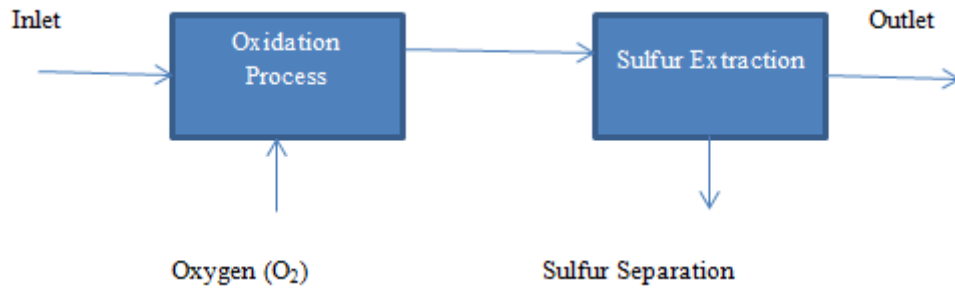


Figure 1: Oxidation Process

Table 1: Sulfur level in crude oil (World Oil Outlook (2011). Vienna, Austria: OPEC Secretariat.)

| Region | 2010 | 2015 | 2020 | 2025 | 2030 |
|-----------|------|------|------|------|------|
| OPEC | 1.38 | 1.36 | 1.39 | 1.45 | 1.49 |
| Non-OPEC | 1.19 | 1.15 | 1.18 | 1.24 | 1.31 |
| The World | 1.00 | 0.94 | 0.97 | 1.03 | 1.13 |

Table 2: World Crude Oil Production (Monthly Energy Review, 2016 (www.eia.gov/mer))

| Region | June 2016 (Million Barrel per day) |
|----------|------------------------------------|
| OPEC | 35.112 |
| Non-OPEC | 31.403 |

1.1 Methodology

The methodology of this study is based on the following procedures:

1. Previous literature reviews and theoretical studies of LCA and desulfurization techniques.
2. Interpretation and assessment of the output inventories of each process (Figure 2).
3. Identification and determination of the influence of each process on the overall results.
4. Best – Worst Case Scenario analysis (Figure 4).
5. Development of a method by using Behnken design for the purpose of evaluating the influence of the factors interaction.

The strategy of the study was to apply LCA for comparison to quantitatively describe and evaluate the impact of selected desulphurisation processes on the environment using the following steps: (1) the goal and scope (2) the life cycle inventory LCI (3) life cycle impact assessment (4) interpretation (Figure 2). In this paper, mass balance theory is applied to estimate the amount of extractive desulfurisation. The inputs of raw materials to an

emission unit are analyzed and account for all possible outputs of raw materials in the form of air missions.

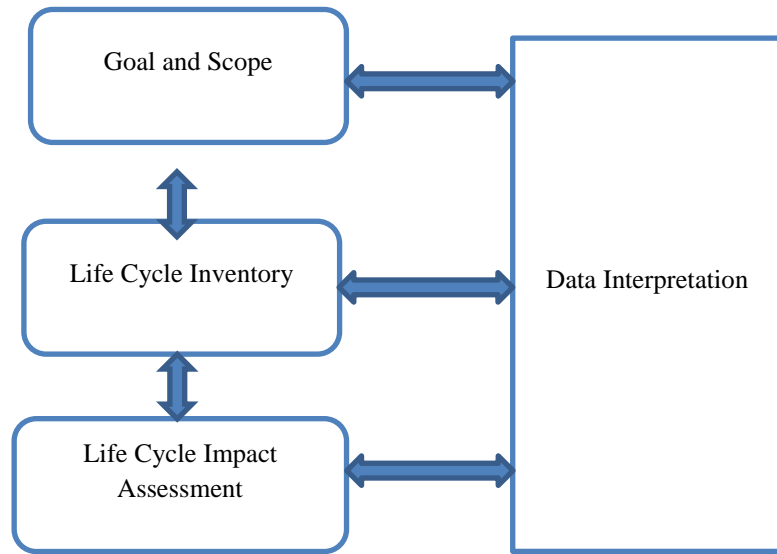


Figure 2: Methodological Framework for Life Cycle Assessment, Revised from [1]

Theoretical desulfurisation technologies were compared quantitatively and assessed each technique based on the energy and material consumption by defining the system boundary and product interaction with the environment (Figure 3).

A measurement of mass unit (g) per unit weight of production (g/unit weight) is chosen, as a reference to measure impact weight of the inputs and the outputs of the process [4]. Furthermore, eco-99 indicators were used to normalize and weigh the environmental damage.

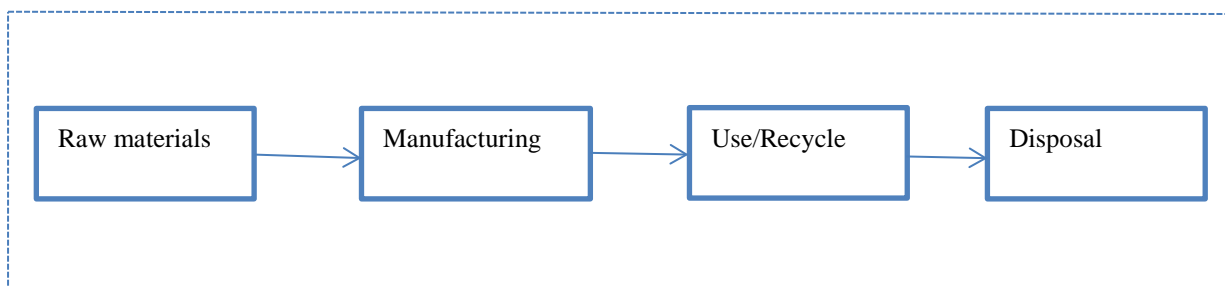


Figure 3: System's Boundry After completing theoretical extraction, the total sulphur content was determined.

1.2 Design of Experiment

The extraction desulfurization model build based on the observed data; the aim of the model is to design a mathematical model describing the extraction model and measuring the effect of their interaction on the extraction performance.

The objective of the design is to be performed to analyse the obtained data, which illustrate an applicable model. Using experimental design (DOE) is a good way to deal with multi-factors. To investigate and determine the impact of the processes, the interaction analysis was design and the most influence design obtained.

The first step in desulfurisation (response) methodology is the development of experimental design by collecting suitable data for each process. The statistical analysis was made using Minitab software. The second step is to carry out the experimental plan and evaluate the impact of the factors (process). This provides important information about each factor for the purpose of the response (efficiency) improvement. Also the model illustrates the influence of the interaction between the main factors. Finally, analysis of variance is determined to estimate the main effect and interaction significance.

The design model for the case of three independent variables is expressed as follow;

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_3x_3 + \varepsilon$$

Y represents the response variable (dependent, desulfurization efficiency)

X represents a predictor variable

β_0 represents a constant (Independent variable)

β_1 , β_2 , and β_3 are regression coefficients

ε represents error term

The study tried to measure the effect of the interaction in first order model

$$Y = \beta_0 + \beta_1x_1 + \beta_2x_2 + \beta_{12}x_2x_3 + \varepsilon$$

2. Environmental Performance Assessment

The Environmental performance evaluation consists of multi-stages: process description, hazard or chemical identification, the impact or severity measurement and the probability of occurrence. A quantitative analysis for environmental performance evaluation purposes is highlighted based on material balance to determine the total effects of the product. The method presented in this paper is to review the overall environmental performance of each method and suggest what action needs to be taken. Figure 4 describes the process methodology used to assess process performance and quantify the weight impact environmentally. Firstly, according to the general process reactions and environmental performance, the pollutant hazard is characterized to determine the risk associated with each process. Finally, risk is identified based on the severity (impact) of the production multiplied by the probability (F). The outcomes of the process given in the final stage lead to continue or stop modification (YES/NO). YES means that the outcome is at an acceptable level and NO means more modification is required. However, the influence of each method was taken as feedback for modifying or

changing to an alternative and reliable process [2]

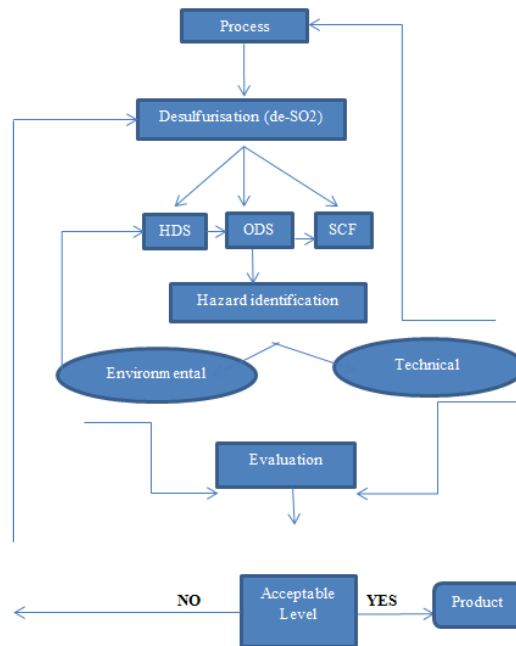


Figure 4: The Methodology Framework for Environmental Evaluation

2.1 The Principle of Assessment

The principle of the assessment aims to provide a quantitative indicator to reduce uncertainties and improve the estimated values. Damage weight of pollutant will also be estimated.

2.2 The Environmental Impact Indicators

There are a number of impact indicators. In this study, the Eco-99 indicator was utilized to convert the mass output of the inventory into concentrations and determine the environmental damage weight for each system or method. Eco-99 is measured based on spatial and temporal calculations; for example, X g CO₂ from a process becomes a mass in a recognized location which disperses at a specific rate over a known time [14].

The objective of the use of the Eco-99 indicator to minimize the uncertainties of damage associated with each pollutant by recognizing the location/space (spatial) and rate/time (temporal).

The outcomes of exposure and effects analysis (damage indicators) are then treated the heading of damage analysis [3, 4].

This means that the consequences of the inventory concentrations are linked to real effects. These enable the damage indicators, which are grouped according to their damage category, to be combined and weighted in the Eco-99 to provide a single value.

The results thus provide a single figure for each material and process that can be used to assess the

environmental damage of the entire product when summed (Table 3). However, there are also uncertainties associated with the indicators provided with Eco-99. To avoid these data fluctuations, a scale is used as an indicator measurement as low as 1 and for the highest impact as high as 5.

3. Process Description

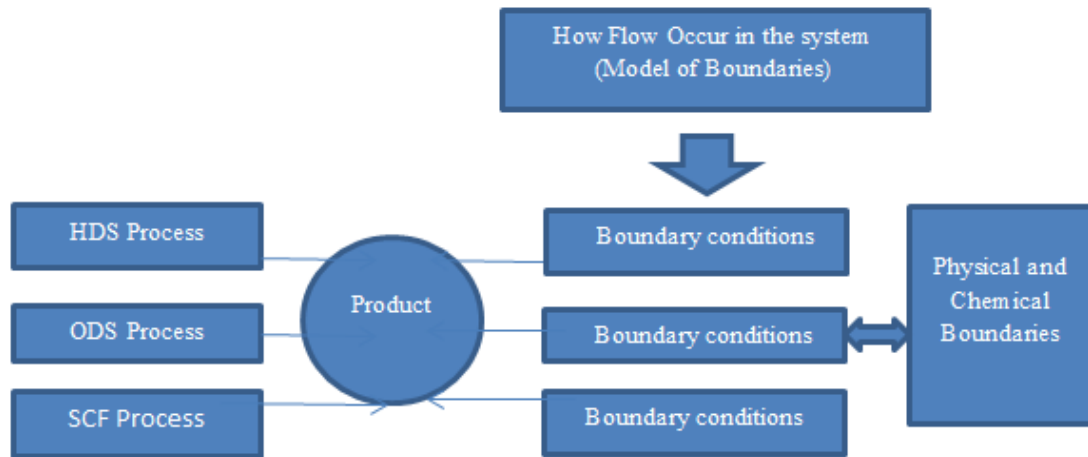


Figure 5: The process strategy for HDS, ODS, and SCF

The desulfurisation production principle is divided into a set of units to convert hydrogen sulfur (H₂S) to elemental sulfur (S).

This study focused on three desulfurisation technologies:

3.1 Hydrodesulfurisation (HDS)

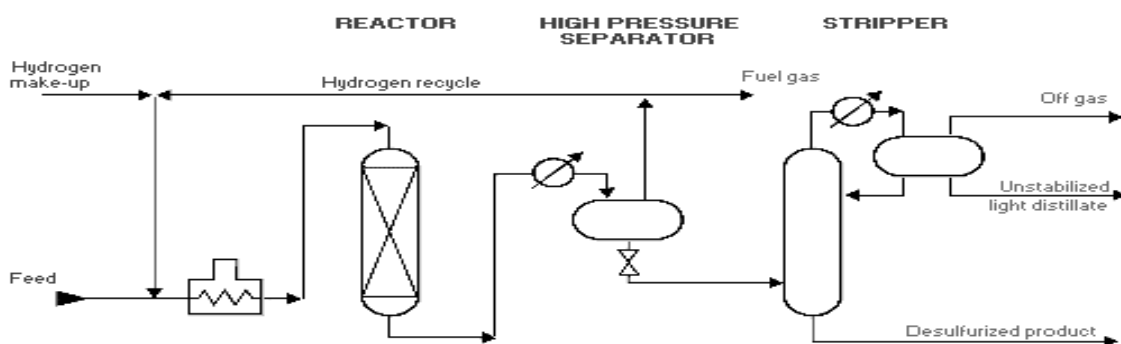


Figure 6: Hydrodesulfurisation Process revised Process, (Reference: (19))

The main objective of the hydrodesulfurisation process is to produce hydrogen sulphide (H₂S) in the presence of hydrogen as follows:

Hydrogenation Reaction



Thiols:



Sulfides:



Disulfides:



R can be the methyl group as methanethiol.

R₁ and R₂ can both be the methyl or carbon group, for example as dimethyl sulphide (R-S-R).

Recovery of sulphur from H₂S

The H₂S produced from the hydrodesulfurisation process is further processed to recover sulfur as elemental sulfur. The overall reactions of the desulfurisation process are described as follows:



To convert H₂S to elemental sulfur, approximately one mole of SO₂ is required.



Reaction (2) shows the combustion step of one-third of H₂S

The overall reaction:



Approximately 50-70% of the H₂S is converted to elemental sulfur. Also, for each 1 kg SO₂ production, there is roughly 0.5-0.7 kg CO₂ emission, which means that further environmental burden in the future associated with sulfur dioxide SO₂ production [4].

3.2 Oxidative desulfurization (ODS)

The main purpose of ODS is to convert the thiols into disulfides using their reaction with a direct or indirect oxidant as follow:



The Sulfur Oxidation:



3.3 Supercritical Fluid Extraction (SFE)

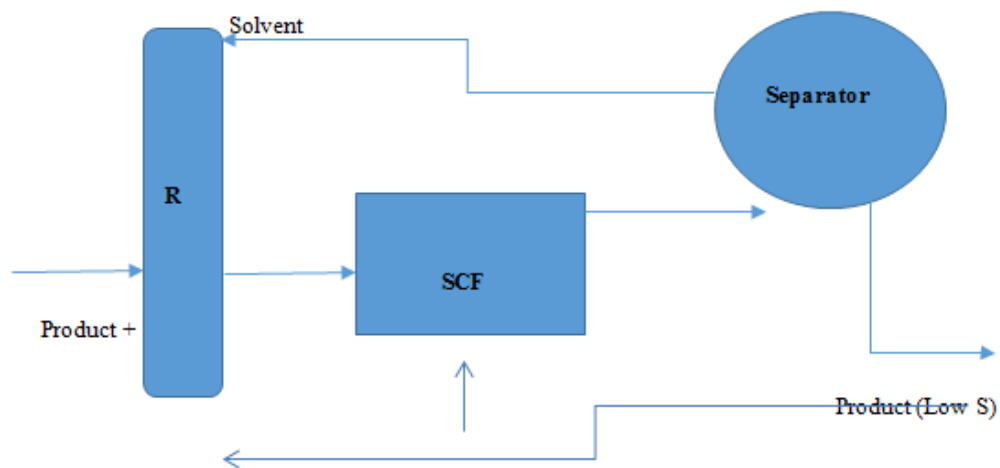


Figure 7: Supercritical Extraction Process (SFE)

The SFE process is described schematically in Figure 7. The process using the CO₂ supply cylinder consists of two steps; the sulfur reaction process, and finally the extraction process step. The supply cylinder contains CO₂. First, the mixture (oil+ sulfur) is fed to the reactor, the scCO₂ at a certain temperature and pressure (t=31.1 OC and 73.1 bars) is mixed with oil and sulfur. In the reactor, sulfur is oxidized to sulfone as described in the following reactions. In this step, separation will take place and sulfur extracted as sulfone and oil, either to be sent back for further extraction to the reactor or collected in the collection vessel as pure product. The following reactions explain the fate of the desulfurisation production of crude oil using the SFE technique:



The reactions above show the desulfurisation process for using scCO₂. It has the potential to oxidize the reactants and convert it to SO₂. Also due to its hydrogenation ability, the formation of hydrogen sulfide (H₂S) takes place, then, sulfur is easily removed from hydrogen by sending H₂S to the Claus Process Unit (CPU) for

further purification.

4. The Production of Manufacturing Materials

The environmental emission category (EE) caused by transport, can be evaluated as follows:

EE = [(System Weight / Capacity of the truck) * Transport distance * Emission factor of the environmental category]

4.1 The Studied Scenario

Approximately 3.8t of fuel (diesel) is consumed to transport 400kg of hydrogen to the plant. A gram of H₂ produces 9 – 12grams of CO₂. About 500,000 Nm³ of H₂ are required per day for purification process (7). According to the chosen functional unit of 3,760kg of electricity is required to operate approximately 200 HDS process system. In this unit process, the following assumptions were applied:

10 tons capacity of a truck

The average distance is assumed to be 200KM

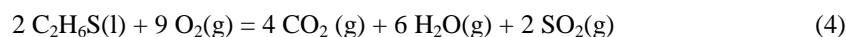
The density of diesel is ($\rho = 0.08 \text{ g/cm}^3$)

The unit of consumption of 10-ton truck is (0.07 L / (t Km) [6]

The energy of consumption can be calculated by the following equation:

The Transportation Energy Consumption = [The weight of the system * Transport Distance * Unit Consumption * Density]

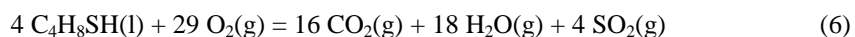
Approximately two tonnes of diesel are consumed to transport 400 kg hydrogen to the plant. While the reaction is proceeding, sulfur compounds, elemental sulfur, mercaptan, thiol, and alkyl are involved. Carbon dioxide results from the chemical reactions as shown in equation 4:



Although desulfurized process takes place, various chemical particles were formed and that increases the output emissions. For example, the formation of disulfide products CS₂ due to the attractive and strong bond between carbon and sulfur as in equation 5.



Also, equation 6 describes the oxidation of thiols. The reaction demonstrates the formation of butanethiol as a result of oxidative reaction.



This scenario showed the influence of the process method on the total production.

5. Characterization

Environmental impact can be defined as the multiplication of the emission by the equivalent factor.

Environmental Impact Potential (EP) = Amount of emission (Q) * Equivalent Factor (EF)

Table 2: Environmental Category Effect

| GW | | AC | | PHCO | |
|-----------------|---------------------|------------------|---------------------|-------------------------------|-----------------------------------|
| Species | Factor kg | Species | Factor kg | Species | Factor kg |
| | CO ₂ /kg | | SO ₂ /kg | | C ₂ H ₂ /kg |
| CO ₂ | 1 | SO ₂ | 1 | CO | 0.03 |
| CH ₄ | 25 | SO ₃ | 0.8 | C ₂ H ₄ | 1 |
| CO | 2 | H ₂ S | 1.88 | CH ₄ | 0.03 |

Table 2 explains the gas emissions equivalent to the chosen reference as CO₂-eq in greenhouse gases (GHG's) and as C₂H₄-eq in photochemical ozone and as SO₂-eq in Acidification due to their life time and the persistency in the atmosphere.

For example, releasing 1 kg of CH₄ into the atmosphere is equivalent to release 25 kg of CO₂.

Table 3: Heat content and energy consumption of Species
 [http://www.eia.gov/totalenergy/data/monthly/pdf/sec13_1.pdf]

| Species | Unit | Quantity[M] * 106 |
|---------------------|-------------|-------------------|
| Petroleum | BTU/ Barrel | 6.024 |
| Hydrogen | BTU/ Barrel | 6.287 |
| Alkane (as Propane) | BTU/ Barrel | 3.836 |
| Sulfur | BTU/ Barrel | 5.77 - 5.83 |
| Oxygenation | BTU/ Barrel | 4.247 |
| Other HC | BTU/ Barrel | 5.825 |

Table 4: Inventory results of oil production [7]

| Item | | Unit | Results |
|----------------------|-----------------|------|----------------------|
| Raw Material | Crude oil | g | 150 |
| | Fuel oil | MJ | 3.37 |
| | Diesel | MJ | - |
| | Electricity | MJ | 15.28 |
| | Water | g | 34000 |
| | Hydrogen | % | - 30 |
| | Oxygen | | (for oil processing) |
| Atmospheric Emission | CO ₂ | Kg | 980 |
| | CO | Kg | 70 |
| | NO _x | Kg | 0.92 |
| | SO ₂ | Kg | 0.88 |
| | HC | kg | 1.56 |

6. Results and Discussion

The inventory of outputs gives the total emission of the production, and the application of material balance helps to evaluate the environmental impact of each method. It also builds a relationship between the energy consumption and the gas emissions which gives the total impact of the system. For example, 1KWh = 3600 KJ electricity, 1 gallon = 13.76 KWh or 1 KWh = 0.07 gallons; where 1 gallon requires 13.76 KWh or 1 barrel requires 578 KWh [3]. Table 4 shows the energy consumption, which can play a significant role, among these methods namely HDS, ODS, and SCF. Since sc-CO₂ utilizes CO₂ which is cost effective of approximately 0.07\$/lb, energy input of 20.689 kwh per 1 lb of CO₂ is consumed. However, H₂ generates approximately 62,000 BTU/lb but carbon generates around 14500 BTU/lb.

It is very observed that the manufacturing process reduces the total energy consumption of SCF due to hydrogen consumption. Approximately 40-50 % reduction of the total emissions can be made. SCF is

economically reliable process and improve the plant safety because it is environmentally-friendly.

Table 6 shows the total energy consumption measured in gram per weight unit of production. The total emission production by SCF has less chemical emissions compared to the HDS and ODS. Nevertheless, SCF has not been commercially utilized for desulfurization of diesel in refineries.

Table 5: The Results of emission inventory of production

| Item | | Unit | Results | | |
|---------------------|------------------|------|----------|---------|-------|
| | | | HDS | ODS | SCF |
| Raw Material energy | Crude oil | g | 1000 | 1000.00 | 17.50 |
| | Fuel oil | MJ | 150,000 | | |
| | Diesel | MJ | 1000.00 | | |
| | Electricity | MJ | 17.50 | | |
| Output Product | Heavy oil | g | - | - | - |
| | Medium oil | g | - | - | - |
| | Light oil | g | - | - | - |
| Emission | CO ₂ | g | 733.33 | 106.67 | 0.580 |
| | CO | g | 54666.67 | 340.00 | 5.826 |
| | NO _x | g | 106.67 | 12.67 | - |
| | SO _x | g | 340.00 | 150.05 | 97.86 |
| | HC | g | 12.67 | 53.54 | 30.30 |
| | H ₂ S | g | 0.580 | 0.342 | 0.254 |
| | HCl | g | 5.826 | - | 2.53 |
| | H ₂ | g | 7330.3 | - | 5.80 |
| O ₂ | g | High | High | - | |

Table 6: Inventory results of desulphurisation per 1 gram diesel for HDS, ODS and SCF

| Compound | Weight(g) | Damage Factor | HDS Impacts | SCF Impacts | ODS Impacts |
|---|-----------|---------------|-------------|-------------|-------------|
| Crude Oil | 1.00E-03 | 5.9 | 5.90E-03 | 5.90E-03 | 5.90E-03 |
| O ₃ | 9.97E-01 | 6.46E-07 | 0.00E-00 | 0.00E-00 | 0.00E-00 |
| SO _x (as SO ₂) | 2.07E+00 | 5.46E-05 | 1.13E-04 | 1.13E-04 | 1.13E-04 |
| H ₂ | 1 | 6.46E-07 | 0.00E-00 | 0.00E+00 | 0.00E-00 |
| O ₂ | 1.19E+01 | 6.46E-07 | 0.00E-00 | 0.00E-00 | 0.00E-00 |
| H ₂ O | 1.10E+01 | 1 | 1.10E+01 | 1.10E+01 | 1.10E+01 |
| Ca(OH) ₂ | 1 | 1 | 1.00E+00 | 1.00E+00 | 1.00E+00 |
| CO ₂ | 3.92E+00 | 1 | 3.92E+00 | 3.92E+00 | 3.92E+00 |
| CaCO ₃ | 1.35E+00 | 1 | 1.35E+00 | 1.35E+00 | 1.35E+00 |
| C ₃ H ₈ | 1 | 7.50E-07 | 0.00E-00 | 0.00E+00 | 0.00E-00 |
| H ₂ S | 0.06 | 5.30E-03 | 3.18E-04 | 3.18E-04 | 3.18E-04 |
| SO ₃ | 0.1127 | 5.46E-05 | 0.00E-00 | 0.00E-00 | 0.00E-00 |
| C ₆ H ₁₂ O ₆ | 1.00E-04 | 1 | 1.00E-04 | 1.00E-04 | 1.00E-04 |
| S ₈ | 2.00E-04 | 5.30E-03 | 0.00E-00 | 0.00E-00 | 0.00E-00 |
| C ₆ H ₁₂ O ₆ | 2.64E-02 | 1 | 2.64E-02 | 2.64E-02 | 2.64E-02 |
| S | 5.64E-02 | 2.60E+02 | 1.47E+01 | 1.47E+01 | 1.47E+01 |
| H ₂ S | 6.00E-02 | 5.30E-03 | 3.18E-04 | 3.18E-04 | 3.18E-04 |
| CS ₂ | 6.70E-02 | 2.60E+02 | 1.74E+01 | 0.00E+00 | 1.74E+01 |
| C ₃ H ₈ S | 5.00E-04 | 7.50E-07 | 3.75E-10 | 3.75E-10 | 3.75E-10 |
| C ₉ H ₁₄ S | 5.00E-02 | 7.50E-07 | 0.00E00 | 0.00E00 | 0.00E00 |
| CH ₃ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₂ H ₅ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₄ H ₈ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₃ H ₁₁ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₆ H ₁₂ O ₆ | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| CO ₂ | 8.70E-03 | 1 | 8.70E-03 | 8.70E-03 | 8.70E-03 |
| H ₂ | 8.52E-04 | 1 | 8.52E-04 | 8.52E-04 | 8.52E-04 |
| C ₂ H ₅ OH | 4.60E-03 | 7.60E-07 | 0.00E00 | 0.00E00 | 0.00E00 |
| C ₇ H ₁₇ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₈ H ₁₇ SH | 6.00E-03 | 7.50E-07 | 0.00E00 | 0.00E+00 | 0.00E00 |
| C ₂ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₁₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₅ H ₁₂ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |

| | | | | | |
|---|----------|----------|----------|----------|----------|
| C ₇ H ₁₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₈ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₉ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₁₀ H ₂₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₃ H ₈ S ₂ | 5.00E-02 | 7.50E-07 | 0.00E00 | 0.00E00 | 0.00E00 |
| C ₄ H ₁₀ S ₂ | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₄ S | 5.00E-02 | 7.50E-07 | 0.00E00 | 0.00E00 | 0.00E00 |
| C ₅ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₆ H ₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₇ H ₁₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₈ H ₁₂ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| Total Impacts | | | 1.92E+02 | 1.88E+02 | 2.05E+02 |

Table 6 gives a description of the environmental emission model for each process. The model is illustrated in the form of a mathematical equation as; Environmental Emission

(EE) = Capacity (C) * Environmental Emission Factor (EF).

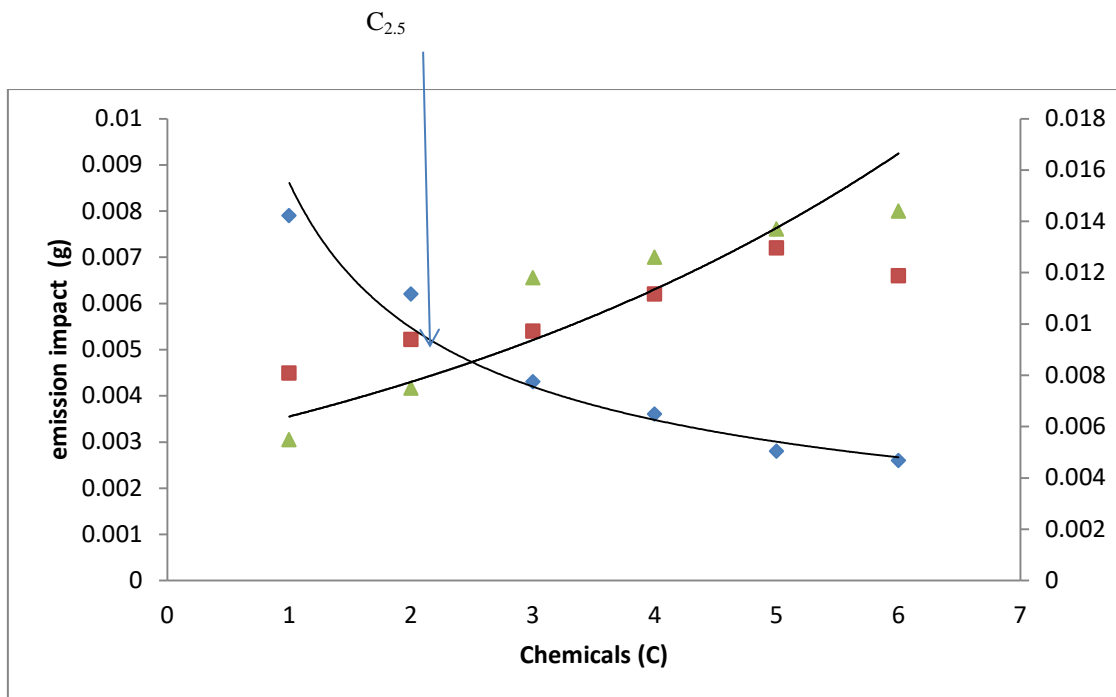


Figure 8: The fate of sulfur-content in the conventional processes

The overall consequences of the methods shown in Figure 8, describes the increases in water vapour and CO₂ emission due to the hydrogen and carbon reactions which take place. However, the parabolic curve gives a

boundary for the process. It shows the maximum allowable level of emissions that needs to be considered. The critical point at C_{2.5} explains the maximum production for best environmental emission reduction that must followed. It ranged between chemical compound C₂ and C₃. These two compounds can be assumed to be located in the zone of mercaptan and thiol (C₂H₅SH, C₂H₆S, C₃H₈S₂, C₃H₈S). It means that Thiophene is an accumulated of these compounds and can be avoided at certain process conditions

Table 7: Categories precursor emissions

| Compound | Weight(g) | Damage Factor | Weighted Damage Factor | HDS Impacts | SCF Impacts | ODS Impacts |
|---------------------------------------|-----------|---------------|------------------------|-------------|-------------|-------------|
| O ₃ | 9.97E-01 | 6.46E-07 | 1.68E-02 | 0.00E00 | 0.00E00 | 0.00E00 |
| SO _x (as SO ₂) | 2.07E+00 | 5.46E-05 | 1.42E+00 | 2.94E+00 | 1.13E-04 | 2.94E+00 |
| H ₂ | 1 | 6.46E-07 | 1.68E-02 | 6.46E-01 | 0.00E00 | 0.00E00 |
| O ₂ | 1.19E+01 | 6.46E-07 | 1.68E-02 | 0.00E00 | 0.00E00 | 7.70E-01 |
| H ₂ O | 1.10E+01 | 1 | 1 | 1.10E+01 | 1.10E+01 | 1.10E+01 |
| CO ₂ | 3.92E+00 | 1 | 5.45E-03 | 3.92E+00 | 8.70E-03 | 3.92E+00 |
| H ₂ S | 0.06 | 5.30E-03 | 1.38E+02 | 3.18E-04 | 3.18E-04 | 3.18E-04 |
| SO ₃ | 0.1127 | 5.46E-05 | 1 | 0.00E00 | 0.00E00 | 0.00E00 |
| S ₈ | 2.00E-04 | 5.30E-03 | 1.38E+02 | 0.00E00 | 0.00E00 | 0.00E00 |
| S | 5.64E-02 | 2.60E+02 | 2.03E+01 | 1.47E+01 | 1.47E+01 | 1.47E+01 |
| H ₂ S | 6.00E-02 | 5.30E-03 | 1.38E+02 | 3.18E-04 | 3.18E-04 | 3.18E-04 |
| CS ₂ | 6.70E-02 | 2.60E+02 | 2.03E+01 | 1.74E+01 | 1.20E+00 | 1.74E+01 |
| CH ₃ SH | 6.00E-03 | 7.50E-07 | 1.95E-02 | 0.00E00 | 0.00E00 | 0.00E00 |
| H ₂ | 8.52E-04 | 1 | 1 | 8.52E-04 | 8.52E-04 | 8.52E-04 |
| Total Impacts | - | - | - | 4.70E+01 | 2.96E+01 | 4.70E+01 |

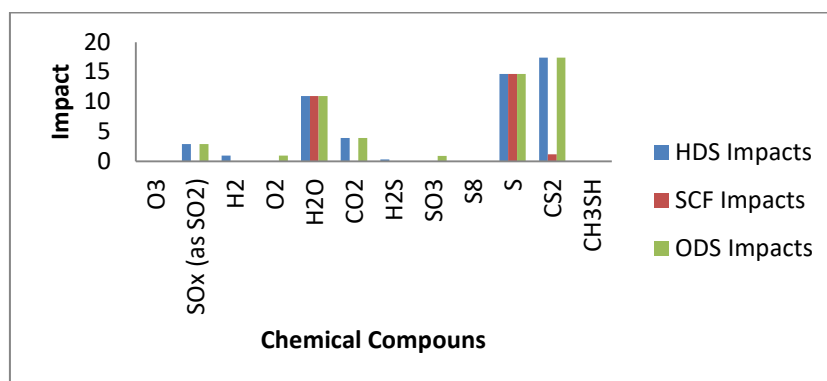


Figure 9: Inventory distribution of each desulfurization method

Table 8: Thiol and Mercaptans resulting from desulfurisation processes

| Compound | Weight(g) | Damage Factor | HDS Impacts | SCF Impacts | ODS Impacts |
|---|-----------|---------------|-------------|-------------|-------------|
| Ca(OH) ₂ | 1 | 1 | 1.00E+00 | 1.00E+00 | 1.00E+00 |
| CaCO ₃ | 1.35E+00 | 1 | 1.35E+00 | 1.35E+00 | 1.35E+00 |
| C ₆ H ₁₂ O ₆ | 1.00E-04 | 1 | 1.00E-04 | 1.00E-04 | 1.00E-04 |
| C ₆ H ₁₂ O ₆ | 2.64E-02 | 1 | 2.64E-02 | 2.64E-02 | 2.64E-02 |
| C ₃ H ₈ S | 5.00E-04 | 7.50E-07 | 3.75E-10 | 3.75E-10 | 3.75E-10 |
| C ₉ H ₁₄ S | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| CH ₃ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₂ H ₅ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₄ H ₈ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₅ H ₁₁ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₆ H ₁₂ O ₆ | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₂ H ₅ OH | 4.60E-03 | 7.60E-07 | 3.50E-09 | 3.50E-09 | 3.50E-09 |
| C ₇ H ₁₇ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₈ H ₁₇ SH | 6.00E-03 | 7.50E-07 | 4.50E-09 | 0.00E+00 | 4.50E-09 |
| C ₂ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₁₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₅ H ₁₂ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₇ H ₁₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₈ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₉ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₁₀ H ₂₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₃ H ₈ S ₂ | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| C ₄ H ₁₀ S ₂ | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₄ S | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| C ₅ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |

The results demonstrate the reliability of using SCF as a benign technology with less environmental damage. Although all methods have removed sulphur at the same extraction level, SCF has significantly reduced sulfur compounds compared to other methods as described in tables 8 and 9.

The limitation of SCF might come from the scale of the process. It may affect the total emission due to the energy consumption.

Table 9: Thiophene emission during the process

| Compound | Weight(g) | Damage Factor | HDS Impacts | SCF Impacts | ODS Impacts |
|---|-----------|---------------|-------------|-------------|-------------|
| CS ₂ | 6.70E-02 | 2.60E+02 | 1.74E+01 | 0.00E+00 | 1.74E+01 |
| C ₃ H ₈ S | 5.00E-04 | 7.50E-07 | 3.75E-10 | 3.75E-10 | 3.75E-10 |
| C ₉ H ₁₄ S | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| C ₂ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₁₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₅ H ₁₂ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₇ H ₁₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₈ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₉ H ₁₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₁₀ H ₂₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₃ H ₈ S ₂ | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| C ₄ H ₁₀ S ₂ | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₄ H ₄ S | 5.00E-02 | 7.50E-07 | 3.75E-08 | 3.75E-08 | 3.75E-08 |
| C ₅ H ₆ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₆ H ₈ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₇ H ₁₀ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |
| C ₈ H ₁₂ S | 5.00E-02 | 2.60E+02 | 1.30E+01 | 1.30E+01 | 1.30E+01 |

6.1 Modeling of the Desulfurization Processes

6.1.1 Statistical Mode

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3$$

Model Summary

Regression Equation in Uncoded Units

$$Y\% = 40.05 + 0.149 \text{ HDS Impacts} + 0.389 \text{ SCF Impacts}$$

Factor Name

X₁ HDS Impacts

X₂ SCF Impacts

X₃ ODS Impacts**Table 10:** The Modeling Design for the coded desulfurization processes

| Run no. | Random no. | X1 | X2 | X3 | Y% |
|---------|------------|----|----|----|-------|
| 1 | 5 | +1 | -1 | 0 | 42.64 |
| 2 | 8 | +1 | +1 | 0 | 50.56 |
| 3 | 7 | 0 | 0 | 0 | 48.13 |
| 4 | 4 | 0 | -1 | +1 | 51.02 |
| 5 | 6 | +1 | 0 | +1 | 58.35 |
| 6 | 3 | 0 | 0 | 0 | 48.15 |
| 7 | 1 | 0 | 0 | 0 | 50.16 |
| 8 | 10 | 0 | -1 | -1 | 64.15 |
| 9 | 2 | 0 | +1 | +1 | 35.12 |
| 10 | 9 | -1 | 0 | 0 | 37.48 |

The purpose of this analysis is use coded values apply the analysis and to determine has the largest influence on the response. Coded values make the analysis very easy since we can remove any term that is not significant without making any change for the model terms Table 10. The impact of each process was determine but this model help to evaluate the impact of these processes on the response (desulfurization efficiency), especially in case of the processes interactions. The above mathematical model describes the extractive desulfurization based on the illustrated data. Using the obtained data, sum of squared, degree of freedom and F-values required for the model and coefficients validation were calculated. Mathematical description of the extractive desulfurization process was expressed with a statistical model obtained from coded values. Using 1+,0,-1 coding coefficients represent the distance between factor levels and the overall mean with higher values marked as +1 ,lower values marked as -1 , where the above tables 7,8, and 9 represent the natural values. It was proven that desulfurization efficiency is proportional to the method option. Because the results based on the type of the process, the maximum and minimum sulfur content depends on the process condition where in this study assumed to be latent variables. The statistical data showed that the most significant effect for process response (efficiency) is the linear effect of X₂, followed by linear effects of X₁ and X₃and the interaction of X₁X₂ which can be demonstrated by the small F-value ($F < 0.05$). The model showing the variability with R². In this study the effects are the type of the unit including HDS (x₁), SCF (x₂), and ODS (x₃) were investigated. Assuming the process condition was kept constant.

Regression Equation in coded Units

Regression Analysis: Y% versus X₂

The regression equation is

$$Y\% = 48.10 - 4.807 X_2$$

$$S = 8.49322 \quad R\text{-Sq} = 16.4\% \quad R\text{-Sq(adj)} = 6.0\%$$

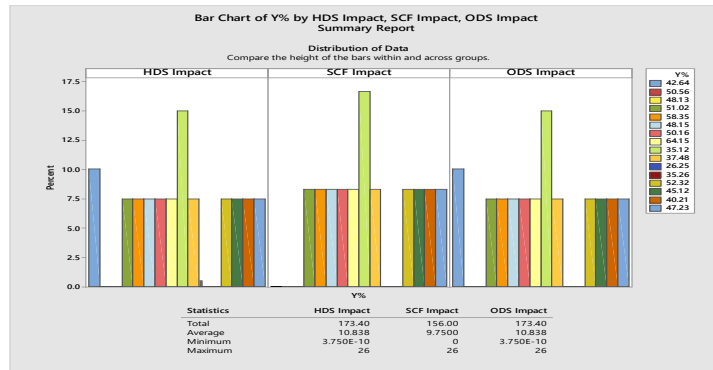


Figure 10: The impact of desulfurisation processes

Analysis of Variance

| Source | DF | SS | MS | F | P |
|------------|----|---------|---------|------|-------|
| Regression | 1 | 113.223 | 113.223 | 1.57 | 0.246 |
| Error | 8 | 577.078 | 72.135 | | |
| Total | 9 | 690.301 | | | |

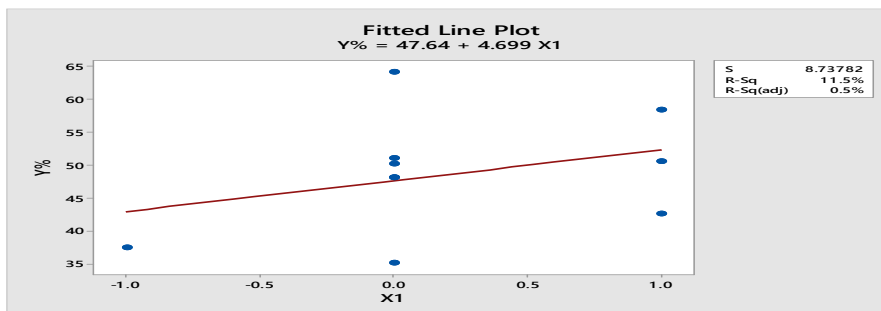


Figure 10: Regression Analysis for HDS, X1

Regression Analysis: Y% versus X₂

The regression equation is

$$Y\% = 48.10 - 4.807 X_2$$

S = 8.49322 R-Sq = 16.4% R-Sq(adj) = 6.0%

Analysis of Variance

| Source | DF | SS | MS | F | P |
|------------|----|---------|---------|------|-------|
| Regression | 1 | 113.223 | 113.223 | 1.57 | 0.246 |
| Error | 8 | 577.078 | 72.135 | | |
| Total | 9 | 690.301 | | | |

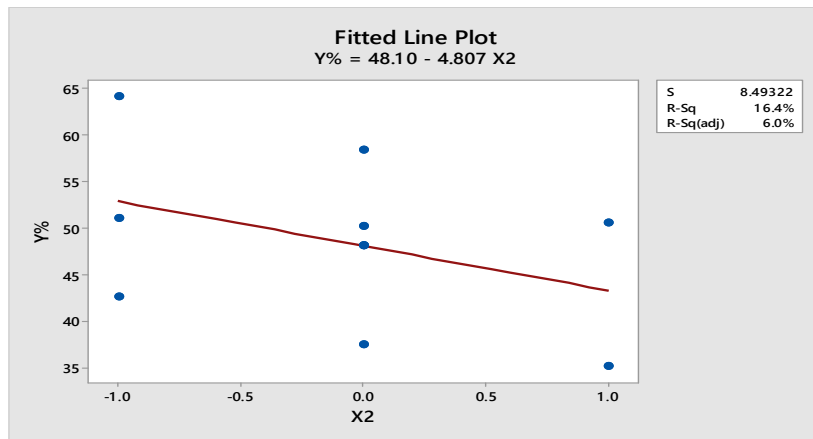


Figure 11: Regression Analysis for SCF, X₂

Regression Analysis: Y% versus X₃

The regression equation is

$$Y\% = 49.51 - 4.670 X_3$$

S = 8.74492 R-Sq = 11.4% R-Sq(adj) = 0.3%

Analysis of Variance

| Source | DF | SS | MS | F | P |
|------------|----|---------|---------|------|-------|
| Regression | 1 | 78.512 | 78.5120 | 1.03 | 0.341 |
| Error | 8 | 611.789 | 76.4736 | | |
| Total | 9 | 690.301 | | | |

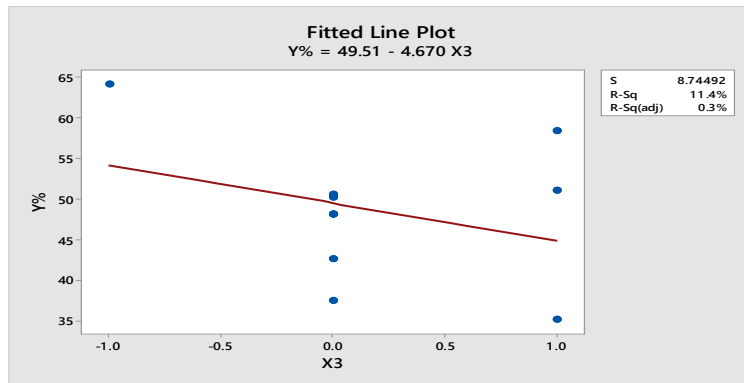


Figure 12: Regression Analysis for ODS, X_3

Best Subsets Regression: Y% versus X_1, X_2, X_3 Response is Y%

| Vars | R-Sq | R-Sq (adj) | R-Sq (pred) | 1 | 2 | 3 |
|------|------|------------|-------------|---|---|---|
| 1 | 16.4 | 6.0 | 0.0 | X | | |
| 1 | 11.5 | 0.5 | 0.0 | X | | |
| 2 | 29.3 | 9.1 | 0.0 | X | X | |
| 2 | 27.5 | 6.7 | 0.0 | X | X | |
| 3 | 37.8 | 6.8 | 0.0 | X | X | X |

The coded results have agreed with the results of three varied processes. It shows that values represent coded units have given the same response (efficiency) of the calculated values (x_1, x_2, x_3) which represent HDS, SCF, and ODS respectively.

7. Conclusions

The life cycle analysis allows us to determine the total environmental impacts of each process. The study has analysed the influence of three desulfurisation methods on the environment by. Theoretically, the process reactions mechanism showed that removal of sulfur compounds still does not reach the optimal goal of emission reduction. Thus, further improvement might be possible for de-SO₂ in order to decrease the threat of the adverse effects of sulfur compounds. To entirely prevent this issue of de-SO₂; the study suggested an alternative way to extract sulfur of SCF. It is an effective way for chemical emission reduction and also saving energy. It also shows the resistance in the processes due to the great solubility of the method for sulfur compounds, and hydrocarbons, that increases the formation of chemical bonds C-C, C-H, C-S, and S-H and produce mercaptan, Thiophene, and thiol. Furthermore, the energy consumption also demonstrated a noticeable risk due to direct and indirect energy uses. The study provides a statistical model to predict the influence of the process and estimate the most influence factor on the desulfurisation. To make a reasonable decision, the analysis illustrated alternative ways for a deep and clean desulfurization method using evaluating interacting effect on the total emission, which is able to cope with unexpected production scenarios. The limitation of desulfurizer process including HDS and ODS has encouraged us to think and search for alternative SCF. Although the study shown that alternative process SCF shown an effective extractive process for sulfur compounds, extending the application on large scale may be difficult. Also detailed researches were not available particularly in SCF to accurately identify and determine the operating condition of alternative SCF as a desulfurizer.

However, the study has recommended several recommendations:

- 1- Further work on the secondary particle forms associated with sulfur production is required to be undertaken in the future researches due to the toxic effect of these chemicals.
- 2- Extending production processes range including HDS, ODS, and SCF over which each process efficiency is valid
- 3- The cost of desulfurisation by SCF is still not known, thus
- 4- Further developing for alternative SCF by designing type of catalyst, temperature, pressure, and appropriate fluid is required for future works.
- 5- It is also suggested that a research performed on mitigating or controlling sulfur compounds in order to investigate and determine their impacts individually on the environment.
- 6- The cost of desulfurisation by SCF is still not known
- 7- Rectifying restricted environmental regulations by authorized institutions that cope with the future changes is recommended, and
- 8- Supporting educational institutions and public education recommended.

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