Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/pc
Petroleum & Coal 50 (3) 1-9, (2008)

STUDY OF THE EFFECTIVE FACTORS IN GASOLINE SWEETENING PROCESS

Saeid Shokri*, Hamid Ganji, Mahdi Ahmadi Marvast, Mansour Bazmi

Research Institute of Petroleum Industry (RIPI), Tehran, Iran, Email:shokris@ripi.ir

Received June 2, 2008, accepted September 5, 2008

Abstract

Low molecular-weight organic sulfur compounds (H_2S, RSH, COS, CS_2) contained in gasoline are major environmental pollutants. The demand for energy in the world is increasing, and therefore the production volumes and processing of sour, mercaptan-containing crude oil are growing in all countries of the world. Because environmental regulation, new processes for hydrocarbon feedstock treatment are more expanding.
Demercaptanization is an appropriate process for sweetening of gasoline. Where, mercaptanic components of gasoline are converted to alkyl disulfides. Simulators are useful tools to manage sweetening operation and to improve the profitability of the process. Based on chemical kinetic and equilibrium data and according to pilot plant data, modeling of the reactors and process simulation were done using HYSYS environment.
HYSYS unit operation extensibility has been used to link Fortran codes for the extractor and regenerator to the HYSYS environment. The effect of different parameters on the process performance has been studied and the process was optimized based on the simulation results.

Keyword: Sweetening; Gasoline; Technology; Sulfur removal; Process; Demercaptanization

---

1. Introduction

Ongoing production from the Iranian crude reservoirs has gradually caused an increase in the sulfur content of the crude. Furthermore, not in a far future, the Iranian sour crude fields will also be producing. Currently there are crude swap agreements between the Islamic Republic of Iran and its neighboring countries and the amount of sour crude fed to the Iranian refineries will be constantly rising.

It would be evident that de-mercaptanization and sulfur removal units will be playing a major role in the future of the Iranian oil and gas industries. Sulfur exists in gasoline in different forms such as pure sulfur, hydrogen sulphide (H_2S), carbonyl sulphide (COS), carbon disulphide (CS_2), mercaptans (RSH) and thiofens. Sulfur content of gasoline causes serious problems because Low molecular weight mercaptans are volatile, highly toxic, corrosive, and have an objectionable odour. High toxicity and volatility of these mercaptans cause serious environmental problems during storage and transportation of such hydrocarbon raw materials.

According to National Iranian Oil Company standard and other international standards, maximum mercaptan content in gasoline has not to exceed 0,23 g/m^3 [6]. Therefore, when the mercaptan content of gasoline is higher than the standard limit, it has to be decreased to allowable amounts. The sulfur or mercaptan reduction of hydrocarbons is called sweetening.

One typical technology employed to remove organic sulfur compounds including mercaptans from petroleum fractions and natural gas streams is the Merox process. This process is being used in some refineries of Iran at present. The required catalyst for the process is of liquid type, which is not available for the refineries because of the US economic sanctions and as a result of a substitute; inferior quality catalyst called LCPS-30 is purchased from the French IFP.

Sulfrex process is another technology similar to that of Merox and has four main sections. The difference between this process and Merox is in the type of catalyst being used.

DMD processes are rather new and are developed in recent 10 years [2-5]. It can be used for demercaptanization of all oil fractions even crude oil. DMD process is composed of four main stages, but there are considerable differences and advantages over the processes described above:

1. Caustic solution is consumed with lower concentration in extraction section. The results are lower consumption of NaOH and no catalyst waste because of entrainment.

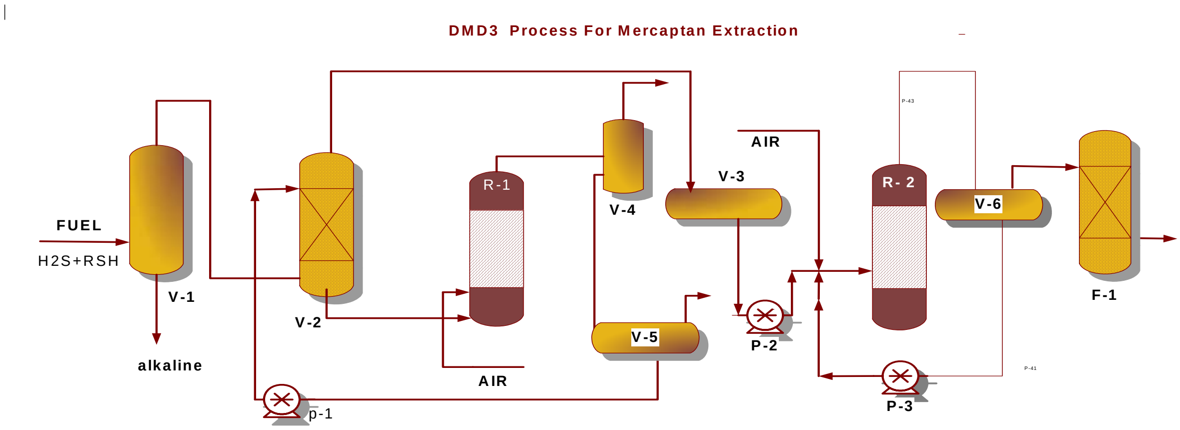
2. The extraction tower of this process is of packed type whose construction is much easier than the tray one of Merox and Sulfrex processes.
3. Fixed bed reactor is also used in the caustic reduction stage and therefore provides the above-mentioned advantages.

2. Process

This process has been designed for demercaptanization of SR gasoline(with distillation range of 62 – 180^{o} C) or cracking gasoline with high mercaptan content. This process is base on removal of low molecular weight mercaptans (methyl to propyl mercaptans) by extraction with aqueous sodium hydroxide and subsequent oxidation of high molecular weight mercaptans to alkyl disulphides. This process reduces the total sulfur content up to 30% and mercaptan content is reduced to 5 ppm. DMD-3 composed of two stages:

1. Extraction (In this section total sulfur and light mercaptan contents is reduced by NaOH.)
2. Sweetening (In this section, the remaining mercaptans that have not been removed by NaOH are converted to alkyl disulphides by oxidation on the catalyst.)

DMD-3 process contains three main parts: Extraction unit, Regeneration unit and Oxidation unit. A schematic diagram of the process is shown in figure (1).



At first, gasoline fraction enters to the bottom of vessel V-1 and hydrogen sulfide and naphthenic acid are omitted by 1-3wt% caustic solution. output gasoline from the top of vessel V-1 enters to V-2 extraction tower. In this tower, low molecular weight mercaptans that are about 50 percent of total mercaptans are omitted. This process is accomplished with caustic solution and catalyst:

$$RSH + NaOH \Leftrightarrow RSNa + H_2O \qquad (1)$$

Output gasoline from this tower enters to surge drum(V-3) and saturated catalyst stream is loaded to the bottom of regeneration tower (R-1) .In This tower NaOH solution in presence of the catalyst and air and at pressure of 4-5 bar is regenerated.

$$2\ RSNa + ½\ O_2 + H_2O \Rightarrow RSSR + 2\ NaOH \qquad (2)$$

From the top of regenaration tower, mixture of catalyst and air are entered to a gaseous seperator (V-4) and air is drained from the top of seperator (V-4) ,from bottom of this vessel, caustic solution with alkyldisulfide are entered in to the disulfide seperator (V-5). In this separator, alkyl disulfide is separated from catalyst mixture. catalyst mixture is then recycled to extraction tower by pump P-1. extracted gasoline from storage tank (V-3) with air and catalyst is sent to oxidation reactor (R-2). In this reactor ,the remained mercaptans are converted to alkyle disulfide. The temperature and pressure of reactor are about 50^{o}C and 10-20 bar respectively . The high pressure is used to dissolve air is gasoline.

$$2\ RSH + ½\ O_2 \Rightarrow RSSR + H_2O \qquad (3)$$

From top of the reactor, demercaptanized gasoline and caustic solution are withdrawn to the V-6 seperator which, gasoline is separated from catalyst that is recycled to the oxidation reactor. Demercaptanized gasoline goes to sand filter (F-1) to discard remained humidity and alkalin material from that.

3. DEVELOPMENT OF MODELS

Three models, comprising a complex set of equations for heat, mass and momentum transfer and the kinetics of the main reactions may be derived to describe the processes in the extractor, regenerator and oxidizer reactor.

The basis of this simulation is based on kinetic and equilibrium data. To becoming familiar with the know-how of this process, a pilot plant is also designed and operated at RIPI. The simulation is completely compatible with the pilot plant design data.

The extraction and regeneration units have been modeled by using the mass and energy balance equations together with reactions kinetics. The model equations have been solved by using Fortran codes.

In order to utilize the HYSYS capabilities, the whole process is simulated with HYSYS except the reaction units (extraction and regeneration) that were simulated separately using the mentioned Fortran codes. It is necessary for the different units of the process to exchange the linked data. For this purpose, the HYSYS EXTENSIBILITY [8] tool is used. Also, a visual basic interface is developed which makes possible the data exchange between Fortran codes and the HYSYS process streams.

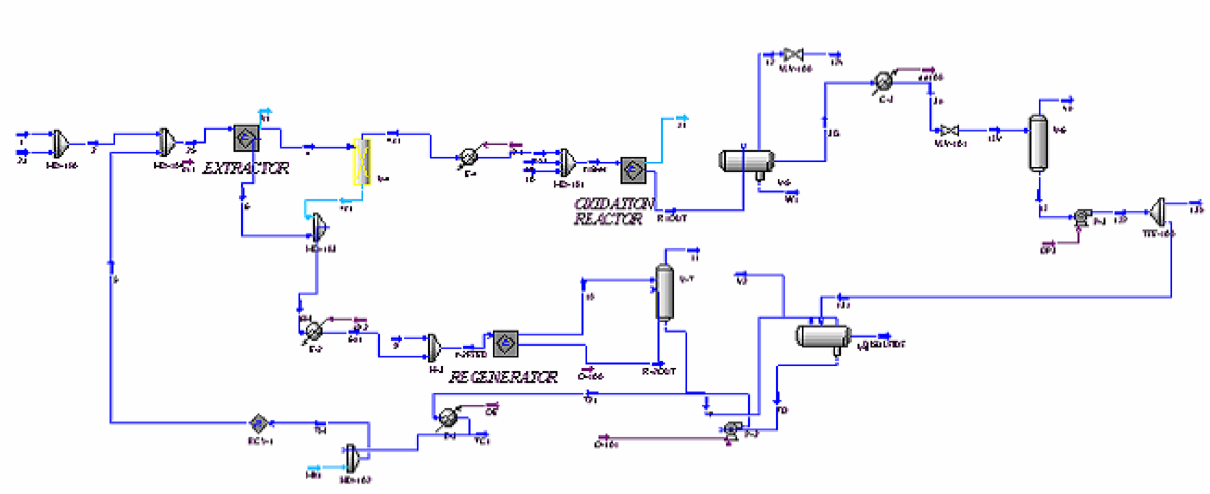


Fig. 1 PFD of DMD3 process (extractor, regenerator and oxidation reactor are shown as extension units).

Table 1 Input gasoline specification: temperature: 30°C, molar flow rate: 0,0484 kgmol/hr, pressure: 6 bar

substance name	molar flow rate(kgmol/hr)	mole fraction	substance name	molar flow rate(kgmol/hr)	mole fraction
n-pentane	0,004348	0,008984	2-methylhexane	0,02454	0,05070
cyclopentane	0,004522	0,009347	n-heptane	0,06941	0,1341
2-methylpentane	0,07916	0,1635	n-octane	0,03125	0,6456
3-methylpentane	0,05431	0,1122	n-decane	0,01338	0,02764
methylcyclopentane	0,02168	0,04479	n-undecane	0,003045	0,006291
n-hexane	0,1371	0,2834	n-propylmercaptane	0,002434	0,005029
cyclohexane	0,01414	0,0292	n-pentylmercaptane	0,001455	0,003006
3-methylhexane	0,0277	0,05724			

A PFD for the DMD3 process is shown in figure 3. Gasoline stream contains n-propyl mercaptan and n-pentyl mercaptan is fed to the process. Gasoline stream's condition is shown in table 1. It first goes to extractor and then to oxidation reactor and regenerator. More detailed information concerning the important components of the process are given below.

3.1 REACTION

In the extractor the reaction is as follows:

$$C_3H_7SH + NaOH \rightleftarrows C_3H_7SNa + H_2O \qquad \Delta H=1{,}2 * 10^5 \text{ J/mole} \qquad (4)$$

It has been found experimentally that the normal pentyl mercaptan does not react significantly with NaOH in the extractor. In the oxidizer reactor. The oxidation reactions are as follows:

$$2\,(C_3H_7SH) + 1/2\ O_2 \longrightarrow (C_3H_7)_2S_2 + H_2O \qquad \Delta H = -1{,}1*10^5 \text{ J/mole} \qquad (5)$$

$$2\,(C_5H_{11}SH\,) + 1/2\ O_2 \longrightarrow (C_5H_{11})_2S_2 + H_2O \qquad \Delta H = -1{,}1*10^5 \text{ J/mole} \qquad (6)$$

In this reactor, normal propyl mercaptan converts to dipropyl disulphide and normal propyl mercaptan converts to dipentyl disulphide.
In the regenerator, sodium propyl mercaptide that comes from extraction is converted in presence of oxygen and catalyst to propyl disulphide.
In the regenerator the reaction is as follows:

$$2\ C_3H_7SNa + 1/2\ O_2 + H_2O \longrightarrow (C_3H_7)_2S_2 + 2\ NaOH \quad \Delta H=-2{,}3*10^5\ J/mole \tag{7}$$

3.2 RATE OF REACTION

Reaction (4) is an equilibrium reaction and its conversion (X) can be determined using the coefficient of mercaptan distribution between two phases [8]:

$$X=\frac{K_d}{1+K_d} \tag{8}$$

$$K_d=\frac{\left[S_{RSH}\right]^{aq.Ph}}{\left[S_{RSH}\right]^{h.Ph}} \tag{9}$$

$[S_{RSH}]^{aq,\ Ph}$ = Mercaptan sulfur concentration in aqueous phase,
$[S_{RSH}]^{h,Ph}$ = Mercaptan sulfur concentration in hydrocarbon phase,
Equations for rate of oxidation reactions (5) , (6) have the following form:

$$\frac{-d\left[RSH\right]}{dt}=\frac{K_1\left[RSH\right]\left[Kt\right]P_{O2}}{1+K_2\left\{\left[RSH\right]_0-\left[RSH\right]\right\}+K_3P_{O2}} \tag{10}$$

[RSH] = Mercaptan concentration, mol/lit
$[RSH]_0$ = Mercaptan initial concentration, mol/lit
P_{O2} = Oxygen partial pressure, atm
[Kt] = Catalyst concentration, mol/lit

The rate of reactions (8) can be expressed by:

$$r_i = A\exp(-E/RT)\,[Kt]\,[RSNa]\,[O_2] \tag{11}$$

where: r_i = rate of i^{th} reaction, mol/(lit.sec), A = pre-exponential factor, lit/(mol.sec), E = Activation energy (J/mol), [Kt] = catalyst concentration, weight percent of catalyst on the surface, [RSNa] = sodium mercaptide concentration, mol/lit, $[O_2]$ = oxygen concentration, mol/lit

3.3 Mathematical Modeling

3.3.1 Liquid Extractor design

Liquid extraction is a process in which solution components are separated by contacting with a solvent. In this process, extract phase is solvent concentrated and component is extracted from Rafinate phase. Usually, solvent phase is considered continuous and feed is considered distributed.
An extractor for DMD process is shown below schematically in fig. 2.
Hydrocarbon feed is entered from bottom and caustic solution from top, reaction takes place and mercaptanes are separated from feed, extractor column can be sieve or packed, In this research sieve tray is considered.

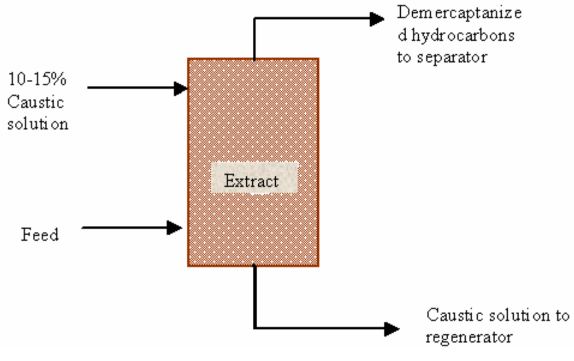


Fig. 2 A schematic of extractor column

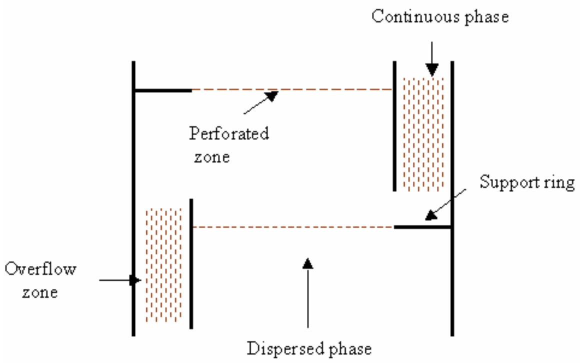


Fig.3 A schematic of column cross sectional area

3.3.2 Column diameter calculation

Column cross sectional area can be divided into three sections as shown in Fig. (2):

1) Perforated zone
2) Overflow zone
3) Support rings

For calculation of column area, the area of these three zones should be calculated.

Perforated area(A_1):

This area can be calculated as below:

$$A_1 = \frac{G}{\rho_d . \varepsilon . W_0} \tag{12}$$

in which, G is mass flow rate of dispersed phase(feed) in kg/sec, ρ_d is dispersed phase density in kg/m^3,W_0 is velocity(m/sec) in holes and ε is holes area per tray area:

$$\varepsilon = \frac{A_0}{A_a} = 0.907(\frac{d_0}{P'})^2 \tag{13}$$

in equation (13), P' is the holes pitch and d_0 is holes diameter,

Overflow area (A_2):

Having continuous phase mass flow and velasity this area can be calculated:

$$A_2 = \frac{L}{\rho_c . V_t} \tag{14}$$

in which L is continuous phase flow(kg/sec**),** ρ_c its density(kg/m$^{3)}$ and V_t is velocity which is obtained from Stokes relation:

$$V_t = \frac{dp^2 \Delta\rho g}{18\mu_c} \tag{15}$$

in eq, (15) dp is droplet diameter(m), $\Delta\rho$ is density difference in two phases, g is gravitational acceleration(m/sec^2) and μ_C is continuou phase viscosity($\frac{kg.sec}{m^3}$),

Support rings area (A_3):

The area of ring section is 10% of the sum of A_1 and A_2 :

$$A_3=0,1(A_1+A_2) \tag{16}$$

Column Height and number of trays:

To calculate the extractor height we can determine number of theoretical trays using Alders formula[ ]:

$$N = \frac{ln(\frac{\varphi - 1}{\lambda\varphi - 1})}{ln\lambda} \tag{17}$$

in this relation φ is fraction extracted:

$$\varphi = \text{Fraction } Extracted = 1 - \frac{X_{iR}.R}{X_{iG}.G} \tag{18}$$

G and R are Feed and Rafinate flow rates respectively, X_{iR} is mercaptane percent in rafinate and X_{iG} is its percent in feed, λ is Extraction factor:

$$\lambda = m\frac{E}{R} \tag{19}$$

m is distribution coficient of mercaptane between phases and E is Extract Flow(kg/hr),
Number of actual trays can be calculated having extractor efficiency(η):

$$N_r = \frac{N}{\eta} \tag{20}$$

we should have tray spacing to calculate the extractor height, Tray spasing is related to column diameter accourding to table (4):

Table 2- column diameter and tray spacing relation

Tower diameter (m)	*Tray spacing (m)*
1 or less	0,50
1-3	0,60
3-4	0,75
4-8	0,90

Height of column is the sum of tray section height , column bottom height(H_b) and height of the top separation section(H_c):

$$H=(TS)(Nr-1)+H_b+H_c \qquad (21)$$

Differential Model:

To calculate mercaptane percent in extract and rafinate phases differential model is used:

$$E_x=\frac{1-exp[N(\lambda-1)(1-z)]}{1-\lambda exp[N(\lambda-1)]} \qquad (22)$$

$$E_y=\frac{1-exp[N(1-\lambda)z]}{\lambda-exp[N(1-\lambda)]} \qquad (23)$$

in Eqs(22) and (23) z is differential dimensionless length and E_x and E_y are extracted component(hear mercaptane) percent in feed and extract phases respectively,

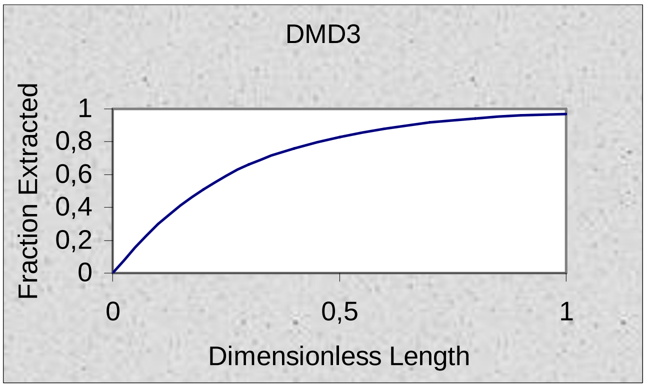


Fig. 4- Fraction of Mercaptane extracted in extractor

3.3.3 REGENERATOR

The modeling of a fixed bed regenerator reactor is presented here, According to the common classification of fixed bed reactor models [11] , one dimensional pseudo homogeneous model is used, In pseudo homogeneous model, conditions within the fluid and solid phases (here bulk gas and catalyst particles) are assumed to be the same, In other words, concentration and temperature gradients occur only in the gas phase

The regenerator is a fixed bed catalytic reactor with 100 mm ID and 1500mm catalyst bed length,

In this model, the following assumptions have been made:

1. The reactor is taken to be under steady state conditions,
2. The model is pseudo homogeneous (i,e, there is no concentration and temperature gradients within the catalyst pellet)
3. There is no radial concentration and temperature gradients in the reactor (i, e, one dimensional model in axial direction),
4. There is no gas radial velocity in the reactor,
5. The radial and axial dispersion has been ignored,

The mass and energy equations for the bulk gas phase (pseudo homogeneous model) can be written as follows:

$$-\frac{d(u_s C_i)}{dl}=\rho_p R_i \qquad i=1,2,\ldots,\ NC \qquad (24)$$

$$\frac{d(u_s\rho_g C_\rho T)}{dl}=\rho_p\sum_{j=1}^{NR}(-\Delta H)_j R_j+\frac{4U}{2\ R}(T_w-T) \qquad j=1,2,\ldots,NR \qquad (25)$$

For the pressure drop, the following equation is used (Ergun Equation [12]):

$$\frac{dP}{dl} = -\left(1.75 + 150\left(\frac{1-\varepsilon_b}{d_p G/\mu}\right)\right)\frac{G^2}{1.01325\times10^6 d_p \rho_g}\left(\frac{1-\varepsilon_b}{\varepsilon_b{}^3}\right) \tag{26}$$

The initial conditions for the bulk phase are given as:

$$l=0, \quad C_i = C_{i,0}; \quad P = P_{in};\ T = T_{in} \tag{27}$$

3.4 The models parameters

The physico - chemical parameters required by the models are introduced in Table 3.

Table 3 Physico – chemical properties estimation methods,

Property	***Method***
Gas viscosity	Lucas [13]
Gas conductivity	Steil – Thodos [14]
Overall heat transfer coefficient	Lovik [15]
Mixed gas heat capacity	Ideal gas [13]
Gas compressibility factor for regenerator reactor inside	Soave-Redlich-Kwong [13]

4. RESULTS

DMD-3 process for demercaptanization of gasoline was entirely simulated by inserting exact models of extractor, regenerator and oxidation reactor models in HYSYS simulation case using HYSYS EXTENSIBILITY tool. The Research Institute of Petroleum Industry (RIPI) has been being involved in DMD-3 technology development for some years. In this regard and in order to get more realistic data and being more familiar with the challenges of DMD-3 plant operation in the pilot scale, a pilot plant has been designed and is being constructed in the RIPI. The pilot plant simulation was done using HYSYS software. The separate Fortran codes written for the reactor simulation were linked to the Hysys environment using the HYSYS Customization tool. The visual basic program interface was used to link Fortran and HYSYS environment.

The operating conditions and sizes of the vessels were considered like those of pilot plant, Input and output parameters for extraction are presented in tables (4), (5). The demercaptanized gasoline specifications are presented in table 9. It is seen that at the end of process all mercaptans (n-propyl mercaptan and n-pentyl mercaptan) has been converted and output stream is a mercaptan free gasoline. Based on the DMD3 pilot plant simulation, parametric sensitivity analysis has been carried out. In this study, the effects of gasoline feed residence time in the regenerator on mercaptans concentration in the treated product have been considered and results are presented in Figures (5), (6), (7), (8).

The objective of this study, as defined by the client, is summarized as follows:

Development of a technical / engineering solution by process simulations that results in optimizing the overall capital expenditure to meet the low sulfur gasoline. The recommended technical approach should be based on proven technology that would minimize the risk to meet the regulatory requirements and maintain a high degree of reliability associated with the selected process.

Table 4- Input parameters

Process	Feed flow(kg/hr)	Extract flow(kg/hr)	Feed density(kg/m^3)	Extract viscosity(pa,s)	% mercaptane in Feed	% mercaptane in rafinate
DMD3	17 583	3 500	664	0,000214	0,1850	0,0051

Table 5- Output parameters

Process	Column diameter (m)	No. real trays	Column height (m)
DMD3	1,1	31	22

Table 6 After extractor

Parameter	Simulation Data	Pilot Plant Data
Temperature (°C)	43,957	41,4
Pressure (kpa)	3200	3050
Molar flow rate (kgmol /hr)	1,251	1,146
COS (kgmol /hr)	0	0
CS$_2$ (kgmol /hr)	6,9185 e^{-6}	5,512 e^{-6}
n-propyl mercaptan (kgmol /hr)	5,6251 e^{-6}	6,215 e^{-6}
n- panthyl mercaptan (kgmol /hr)	3,7724 e^{-6}	3,941 e^{-6}
H$_2$O (kgmol /hr)	0,22197	0,237
NaOH (kgmol /hr)	2,2089 e^{-2}	2,846 e^{-2}

Table 7- Gasoline demercaptanized specification

Parameter	Simulation data	Pilot plant data
Temperature (°C)	30,287	30,8
Pressure (kpa)	4500	4545
Molar Flow Rate (kgmol /hr)	0,48079	0,5120
n-propyl mercaptan (kgmol /hr)	3,6251e^{-6} (4 ppm)	3,925 e^{-6} (4 ppm)
n- panthyl mercaptan (kgmol /hr)	7,8567e^{-6} (8 ppm)	7,986 e^{-6} (8 ppm)
COS (kgmol /hr)	0 (0 ppm)	0 (0 ppm)
CS$_2$ (kgmol /hr)	6,9185e^{-6} (8 ppm)	5,854 e^{-6} (6 ppm)

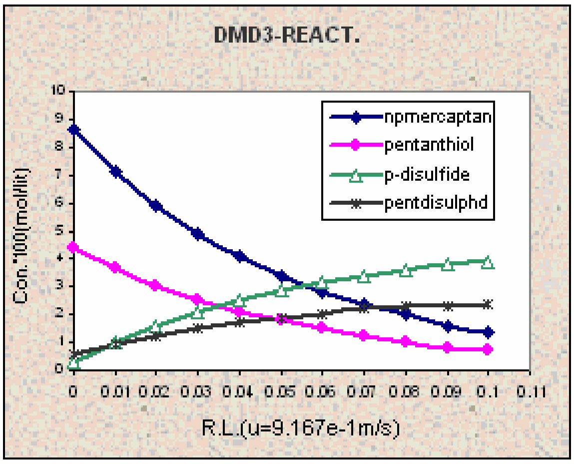


Fig. 5 Effects of gasoline feed residence time in the reactor on mercaptans concentration in the treated product

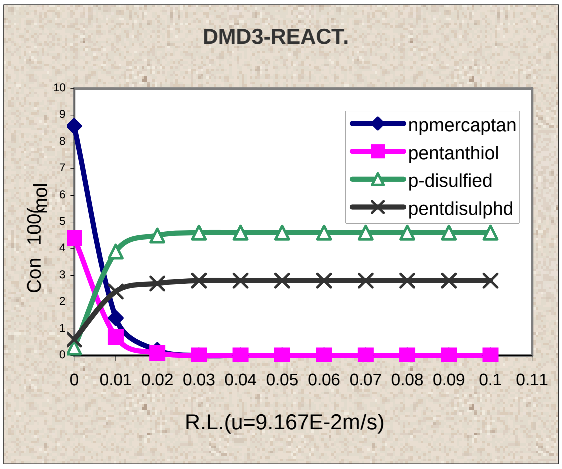


Fig. 6 Effects of gasoline feed residence time in the reactor on mercaptans concentration in the treated product

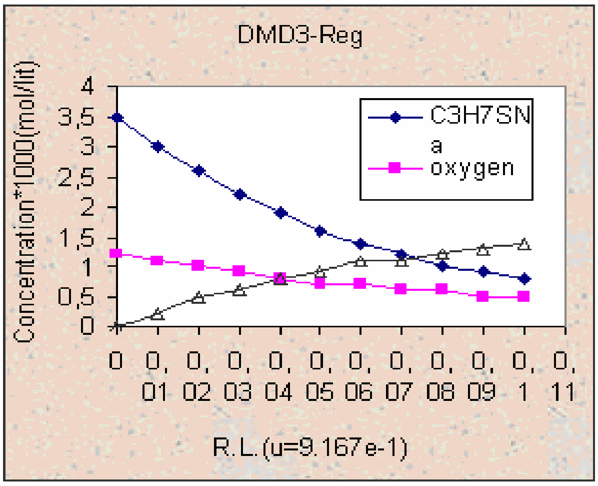


Fig. 7. Effects of gasoline feed residence time in the regenerator on mercaptans concentration in the treated product

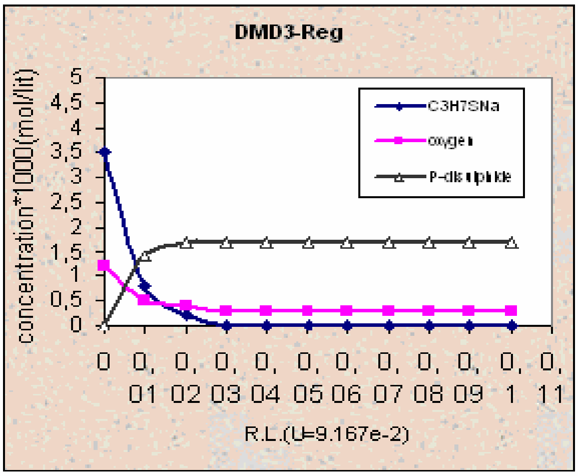


Fig. 8. Effects of gasoline feed residence time in the regenerator on mercaptans concentration in the treated product

NOMENCLATURE

C_i = concentration of component i, mol / m^3
Ci, 0 = initial concentration of component i, mol / m^3
C_p = heat Capacity, J / Mol, K
D_{out} = outlet Diameter of the reactor

d_p = equivalent diameter of catalyst particle
G = mass flux of flowing fluid, kg / m_2 S
ΔH = heat of reaction, J / Mol
l = reactor length, m
P = pressure, bara
T = temperature, K
T_o = inlet fluid temperature to the reactor, K
U = overall heat transfer coefficient,
u_s = superficial velocity of fluid through the reactor, m / S
ε = bed void fraction
η = effectiveness factor
μ = viscosity of the fluid, kg / m, S
ρ_b = bulk density, kg / m^3
T = temperature, K

REFERENCES:

[1] BP Statistical Review of World Energy, June 2004, Could be accessed via internet
[2] A. M. Mazgarov, A. F. Vildanov, N. G. Bazhirova, G. B. Niamutdinova, S. N. Sukhov ; US. Patent 5,683,574; Nov. 4, 1997,
[3] A. M, Mazgarov, A. F. Vildanov, N. G. B. Dinova; U, S, Patent 5,849,656; Dec, 15, 1998,
[4] A. M, Mazgarov, A. F. Vildanov, N. G. Bazhirova, G. B. Niamutdinova, S. N. Sukhov; US. Patent 5,880,279; Mar. 9, 1999,
[5] A. M. Mazgarov, A. F. Vildanov, L. W. Jossens; “ A Selective Treatment of Various Oils and Gas Condensates to Remove Light Mercaptans and Hydrogen Sulfide”; Presented at World Petroleum Congress; Beijing, China; 1998,
[6] Product Specification, MOGAS 200; NIORDC (National Iranian Oil Refining & Distribution Company); Iran, 1999,
[7] “Investigation of desulfurization methods for oil fractions”, NIOC, RIPI , Internal Report, Iran
[8] Hysys Process “Customization Guide” manual; 1998 Hyprotech Ltd,
[9] W. L. Nelson, “Petroleum Refinery Engineering” ,5th edition, 1993, MC Graw-Hill,
[10] Technical information from TATNEFT, Russia,
[11] G. F. Froment; Fixed bed Reactors, Technological and Fundamental Design Aspects; Chemie-Ing Techn; 46, 374 – 386, 1974,
[12] S. S. E. H. Elnashaie and S. S. Elshishini; “Modeling, Simulation and Optimization of Industrial Fixed Bed Catalytic Reactors”; Gorden and Breach Science, 1993,
[13] Bruce E, Poling, John M, Prausnitz, John P, O'Connell; "The Properties of Gases & Liquids", 5th edition, 2001,
[14] Robert H. Perry, Don Green, 1984, "Perry's Chemical Engineering Handbook", 6th edition,
[15] Lovik, I., (2001),"Modeling, Estimation and Optimization of the Methanol Synthesis with Catalyst Deactivation", PhD thesis, Norwegian University of Science and Technology,
[16] Curtis F. Gerald and Patrick O. Wheatly; “ Applied Numerical Analysis”; Addison Wiley, 4th Edition; 1989