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Model and Simulation of the Oxidation Reactor for Oil Refining

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Abstract: Chemical reactors in the industry had been widely used due to his main functionality of control the chemical reactions through his design in order to promote a specific reaction between multiple options. To achieve the objective, it is necessary the knowledge of physicochemical properties of each compound present at the in and out flow of the reactor. To predict these properties, it was used the Peng-Robinson equation of state, the inlet flow was obtained from the residues of an atmospheric distillation column of crude oil which were completely oxidized to their more stable state. Furthermore, a brief design of the reactor was made to develop the reactions. Finally, to resume the calculations of the reactor, the main operational features were characterized, to obtain a mathematical correlation of each variable for the purpose of facilitate the control of the reactor.

INTRODUCTION

Chemically, the oxidation process refers to the actions of whereby apparently an atom or ion loss or share electrons. In early times, this definition was only made for reactions with oxygens wherever it was found that non-metallic elements react in the same way as the oxygen do[1, 2].

One of the processes more examined of oxidation was the mixture of oxygen with other elements through a chemical reaction, due to the oxygen is one of the more abundant elements on Earth[3]. For example, the metal oxidation to generate rust or the combustion of carbon chains to form Carbon dioxide (CO_2). That involve the generation of two oxidation categories, the fast and the slow. The slow oxidation was assigned to natural processes that are very slow as the wood oxidation, the respiration process or putrefaction of organic compounds. Wherever, the slowness of the process generates that the energy produce be dispersed in the environment[1, 4].

The fast oxidation produces visible effects in short time, as the production of energy in the form of heat, who increase the environment temperature, par example, the burn of fossil fuels[5, 6]. This kind of reactions are also named combustion reactions.

In the petroleum refining, the oxidation reaction is applied to the residues obtained from the plant in order to decrease the contamination and the damage to the environment. The main products of this process are the generation of carbon dioxide, carbon monoxide and some oxides of metal[1, 7, 8].

Because they are fast oxidation reactions, the quantity of heat generate to the environment is high. This energy is usually used to warm up fluids in the sub processes of refining. From the data obtained in the phase 1 of the project and the characterization of the crude in the distillation column, it was developing a process for the utilization of the residues from the fractioned distillation column, through reactions of oxidation to the present compounds.

MATERIALS AND METHODS

The stream used is shown in the Table 1. To achievedthe oxidation process, it was necessary an oxygen stream with a uniform distribution in the reactor. Furthermore, a stream of steam and other of fuel are needed. For the oxidation process, it was determined each one of the inlets necessaries for reactor operation, between them was the combustible, who was used to promote the burst of the system, additionally keep the flame burning. For this case, the fuel used was methane whereby to keep the flame the flux was 0.016 kg/h which are equivalent to 1 mole/h.

The fast oxidation reactions Fig. 1 could have two main products who have a dependency with the amount of oxygen present in the environment at the moment of the combustion.

To determine the priority of the combustion reactions, it was determined the Gibbs free energy which is an extensive relation of the energy of a substance which represent the chemical equilibrium or the spontaneity or a reaction. The Gibbs free energy (G) was defined as a relation between the enthalpy (H) and entropy (S) of a substance Eq. 1[9]:

$$G = H\text{-}TS \tag{1}$$

$$aA+bB \rightarrow cC\text{-}dD\ \Delta G_{rxn} = \left(c*\Delta G_C+d*\Delta G_D\right)\text{-}\left(a*\Delta G_A+b*\Delta G_B\right) \tag{2}$$

where, T was the temperature of the system. For a chemical reaction, it was determined the change in the Gibbs free energy to determine the equilibrium direction Eq. 2. If the value is negative, the process is spontaneous, if it is positive, the reaction requires energy while if the value is zero, the reaction is in chemical equilibrium. For production of carbon dioxide from methane:

$$CH_4+20_2 \rightarrow CO_2+2H_2O$$

$$\Delta G_{rxn} = \left(\Delta G_{CO_2}+2*\Delta G_{CH_4}+2*\Delta G_{O_2}\right)$$

$$\Delta G_{CH_4 \rightarrow CO_2} = \text{-}818.255\frac{kJ}{mol}$$

For carbon monoxide:

$$2CH_4+30_2 \rightarrow 2CO+4H_2O$$

$$\Delta G_{CH_4 \rightarrow CO} = \text{-}561.048\frac{kJ}{mol}$$

The values of the Gibbs free energy for the substances used were taken from[9-12]. Due to these are fast reactions, the equilibrium will be governed by the availability of oxygen in the reactor. For the purpose of conduct the equilibrium to formation of carbon dioxide, the inlet oxygen in the reactor correspond to 1.7 times the required oxygen, through different mechanical elements who facilitate the mixture.

Even so, to take into account the two main reactions, it was assigned a possibility of occurrence taking as base the Gibbs free energy for each reaction Eq. 3:

$$P_{A \rightarrow B} = \frac{\Delta G_{A \rightarrow B}}{\Sigma\left(\Delta G_{A \rightarrow \ldots}\right)} \tag{3}$$

$$P_{CH_4 \rightarrow CO} = \frac{\Delta G_{CH_4 \rightarrow CO}}{\Delta G_{CH_4 \rightarrow CO}+\Delta g_{CH_4 \rightarrow CO_2}}$$

$$P_{CH_4 \rightarrow CO} = 0.407$$

$$P_{CH_4 \rightarrow CO_2} = 0.593$$

Hence, the 40.7% of the inlet methane will be turned in carbon monoxide while the remaining will produce carbon dioxide. A complete reaction of chemical reagents is ensured due to the oxygenexcess, the mechanical design of the reactor and the temperature and pressure inside himself.

The residues stream consists of the substances in Table 2, the previous procedure it was followed for the alkanes, however it is important highlight the metals present which react in presence of oxygen an steam. The products obtained by the oxidation of metal in the residues stream were in Table 3, moreover the final products of sulfur were shown. It should be noted that sulfur had more complex reactions tan the other elements as shown below:

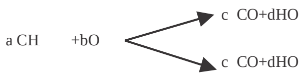

Fig. 1: Oxydtion reactor

Table 1: Properties of residues stream from the fractioned distillation column

Properties	Values
Extraction tray	61
X	0.000
Temperature [°C]	794.4
Pressure [kPa]	1400
Flux [kg/h]	2619.59
API	-2.654
Sulfur (%w)	2.627
Cp prom [kJ/mol k]	24.147
Kinematic viscosity [cSt]	1693.67

Table 2: Residues stream from the atmospheric distillation column

Compounds	Flux [kg/h]
Ethane	0.300
Propane	0.104
n-Butane	0.293
n-Pentane	0.391
n-Hexane	1.524
n-Heptane	1.713
n-Nonane	3.590
n-C12	3.870
n-C16	9.851
n-C20	486.216
n-C24	909.230
n-C28	2582.682
n-C32	1914.465
n-C36	438.976
Metals	1.546
Sulfur	68.817

Table 3: Metals oxidation products

Elements	Product	Delta G° [kJ/mol]
V	V_2O_5	-1439.980
Ni	NiO	-216.300
Ni	$Ni\ (OH)_2$	21.016
Ni	$Ni\ (OH)_3$	-
Na	Na_2O	-376.990
Na	Na_2O_2	-379.250
Na	NaOH	-182.192
Fe	FeO	-248.560
Fe	Fe_2O_3	-742.200
Fe	$Fe\ (OH)_2$	-9.964
Fe	$Fe\ (OH)_3$	16.664
Al	Al_2O_3	-1577.160
Mg	MgO	-570.000
Ca	CaO	-604.050
Ca	CaO_2	-598.998
Ca	$Ca(OH)_2$	-395.914
S	S_2O_3	-
S	SO_4	-

$$S^{2-}+2O_2 \rightarrow SO_4 \quad 2SH^{-}+2O_2 \rightarrow S_2O_3^{2-}+H_2O$$

Furthermore for these reaction were not found the theoretical values for Gibbs free energy, due to, there were experimental values from equilibrium at[1] p.1265. Another factor to take into account in the reactor was the energy produce by the reactions, reason why an energy balance was made.

$$Q+W = m*g*\left(z_2-Z_1\right)+\left(H_2-H_1\right)+\frac{1}{2}*m*\left(V_2^2-V_2^2\right)$$

For this process, the potential and kinetic energy were negligible with regard to the internal energy of the system. Additionally, there wasn't work at the reactor, reason why the energy balance could be resumed in Eq. 4 where the heat generated depend on the difference between the reactions enthalpy:

$$Q = \left(H_2-H_1\right)$$

Table 4: Heat capacity coefficients for methane in function of temperature[12, 13]

Specie	Delta H° 298 [kJ/mole]	A	B	C	D
CO_2	-393.509	5.45	1.05E-03	----	1.16E+05
O_2	0.000	3.63	5.06E-04	----	2.27E+04
H_2O	-284.650	3.47	1.45E-03	----	1.21E+04
CH_4	-74.870	1.70	9.08E-03	-2.16E-06	----

To made the enthalpy calculus, a reference state was determined for this case, it was defined at 1 atmosphere and 298.15 k. Due to the reactor temperature is higher than reference temperature, it was established the change in the enthalpy from the reference state to the reactor state for changes in the same phase it was used the Eq. 5.

$$\begin{aligned}
\frac{d\Delta H^{o}}{dT} &= \sum_{i} m_i * \frac{d\bar{H}_{\iota}}{dT} \\
\frac{d\Delta H^{o}}{dT} &= \sum_{i} m_i * \overline{Cp_{\iota}^{o}} \\
\Delta H^{o} &= \sum_i m_i * \int_{T_1}^{T_2} \Delta CP^{o} dT
\end{aligned} \tag{5}$$

$$Cp = \left(A+BT+CT^2+\frac{D}{T^2}\right)*R$$

Where:

Cp = Heat capacity of the substance
R = Ideal gas constant (8.314 J/mole k)
A-D = Constants for each compound

Table 4 are the coefficients necessary to determine the change in the heat capacity, to determine the energy produce by the methane combustion at 363.15 k. For negative values of enthalpy, the reaction generate heat while for positive values the reaction need energy. The change in enthalpy was made via. Eq. 5:

$$\Delta H_{rxn} = \left(\Delta H_{CO_2}+2*\Delta H_{H_2O}\right)-\left(\Delta H_{CH_4}+2*\Delta H_{O_2}\right)$$

The above procedure was used for every reaction made in the oxidation reactor. Due to, the reactions were exothermic, the reactor was designed with a cooling system in order to keep the temperature stable. For this case was recommended used a thermic oil, to improve the heat transfer. The oil flux was determined through an energy balance of the heat generated in the reactor.

To realice the process control, the mathematical model was obtained, however for this process, therewere a lot of variables from the multiple reactions, who influent the behavior of the reactor. In order to decrease the complexity of itself, it was taken the principal variables with was made their respective regressions, from the obtained data. The models were:

- Generated energy by the metal oxidation according to the reactor temperature
- Generated energy by the alkane oxidation according to the reactor temperature
- Total generated energy by oxidation according to reactor temperature
- Total generated energy by oxidation according to residues flux from the distillation column
- Refrigerant flux according to reactor temperature
- Oxygen necessaire according to residues flux from the distillation column
- Steam necessaire according to residues flux from the distillation column

To obtain each model the other variables were stationary, according to the values for steady state in the reactor. To obtain the regression, the toolbox curve fitting from matlab was used.

RESULTS AND DISCUSSION

In Table 5 were shown the flux involved in the reactor for the fuel methane. It should be noted that the reaction for this compound was complete following the reaction probabilities according to the Gibbs free energy and the excess of oxygen which move the equilibrium as explained before. For the other substances from the residues stream, the probability of reaction was determined. In Table 6, there was a brief of the reaction involved at the reactor.

It is worth nothing that substances with only one product had a reaction probability of occurrence of 1, due to the mechanical design of the reactor in which all the inlets compounds will be fully oxidize. In Table 7 were shown the reactor outlet stream in steady state at 263.15k and 7.6 bar.

It is also, important thing that the output stream from the reactor had more of the 34% of oxygen, reason why in order to increase the profits in the system, it is necessary to develop and implement an oxygen recovery system. Furthermore, the ratio between dioxide carbon and monoxide carbon was almost 2.6 times whereby the goal of move the equilibrium through a full oxidation was achieved.

This was made via the adjustment of some elements mechanicals in the reactor Fig. 2, as they were the inlet division of oxygen. Each input current had a tray metallic with sieves which distribute and enhance the contact area between the residues stream with the oxygen. In addition, a package zone equivalent at 10% of the reactor was added in order to encourage the conversion of reagents.

The output stream reactor had a pump to enhance the displacement of matter and give the necessary pressure to send the fluid to the separator. It should be noted that inside the reactor there was a mixture of substances in different phases. The forced departure of the fluid at the bottom of reactor by the pump, increase the mixture and recirculation of the inlet gases. With the purpose of increase the residence time and the reagents conversion.

Table 5: Methane for fuel stream

Components	In flux [kg/h]	Out flux [kg/h]
Methane (CH_4)	0.016	----
Oxygen (O_2)	0.097	0.040
Carbon monoxide (CO)	----	0.011
Carbon dioxide (CO_2)	----	0.026
Water (H_2O)	----	0.036

Table 6: Reaction probability for the oxidation reactor

Reagent	Product	Probability	Reagent	Product	Probability
Butano	CO_2	0.615	V	V_2O_5	1
	CO	0.385	Ni	NiO	0.911
Pentano	CO_2	0.617		Ni $(OH)_2$	0.044
	CO	0.383		Ni $(OH)_3$	0.044
Hexano	CO_2	0.619	Na	Na_2O	0.402
	CO	0.381		Na_2O_2	0.404
Heptano	CO_2	0.62		NaOH	0.194
	CO	0.38	Fe	FeO	0.244
Nonano	CO_2	0.621		Fe_2O_3	0.73
	CO	0.379		Fe $(OH)_2$	0.0
$C_{12}H_{26}$	CO_2	0.622		Fe $(OH)_3$	0.016
	CO	0.378	Al	Al_2O_3	1
$C_{16}H_{34}$	CO_2	0.623	Mg	MgO	1
	CO	0.377	Ca	CaO	0.378
$C_{20}H_{44}$	CO_2	0.623		CaO_2	0.375
	CO	0.377		Ca $(OH)_2$	0.248
$C_{24}H_{50}$	CO_2	0.624	S	S_2O_3	0.66
	CO	0.376		SO_4	0.34
$C_{28}H_{58}$	CO_2	0.624	Etano	CO_2	0.606
	CO	0.376		CO	0.394
$C_{32}H_{66}$	CO_2	0.624	Propano	CO_2	0.612
	CO	0.376		CO	0.388
$C_{36}H_{74}$	CO_2	0.624			
	CO	0.376			

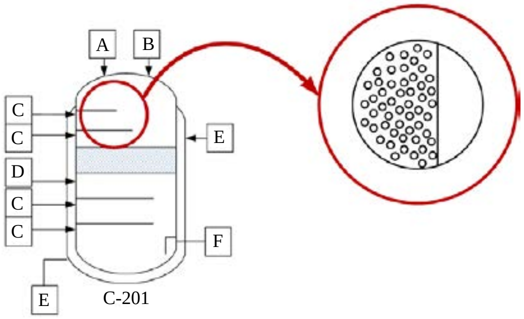

Fig. 2: Oxydation reactor; A = Residues inlet stream from the fractionated distillation column; B = Fuel inlet stream (Methane); C = Oxygen inlet stream; D = High steam inlet. E = Refrigeration oil; F = Output flux from the reactor

Table 7: Output flux from the oxidation reactor

Flows	Values (kg/h)
Total	15884.539
CO	1907.217
CO_2	4975.281
H_2O out	3388.534
Metals oxides	152.117
H_2	0.001
O_2 excess	5461.389

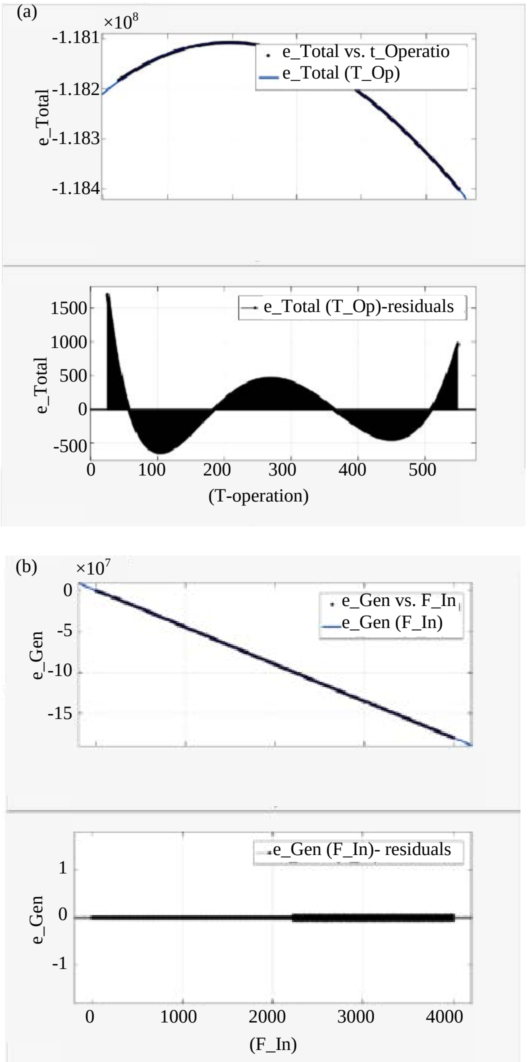

Fig. 3(a-b): Equation and error for each type of relation. (a) Where the operation temperature was involved; b) Where the flow was involved

To refrigerate the reactor, the cooling oil pass through a shell reactor because, it had a better stability according to the temperature. It was used the Dowtherm RP Heat Transfer Fluid where with were calculated the characteristics for a steady state in Table 8. It is important to note that the heat retired from the reactor had an important value, reason why, to decrease the cost in the plant, the heat could be used to warm up another fluid.

Table 8: Cooling refrigerant

Parameters	Values
Flow [kg/h]	2009376
Inlet temperature [°C]	25
Heat capacity [kJ/kg k]	1.6798
Outlet temperature [°C]	60
Heat [kJ/h]	-1.18E+8

Table 9: Model for selected variables at the oxidation reactor

Functions	Equations
E_Metal (T_Op)	$f(x) = -83.53*x-1.294e+06$
E_Alcano (T_Op)	$f(x) = 1.057e-06*x^4-0.0005086*x^3-2.53*x^2+1103*x-1.169e+08$
E_Total	$f(x) = 0.0007011*x^3-$
$2.989*x^2+1085*x-$	
(T_Op)	1.182e+08
E_Total	$f(x) = -4.51e+04*x+0.001063$ (F_In)
F_Ref	$f(x) = 3.837e-06*x^4-0.007439*x^3+$
O_2_In	$f(x) = 5.063*x+0.09774$ (F_In)
H_2O_In	$f(x) = 1.42e-05*x+5.065e-13$ (F_In)

Table 10: Error for each prediction

SSE	R^2	RMSE
2.89E+06	1	33.19
2.43E+06	1	30.48
4.72E+08	1	424.2
7.51E-01	1	0.01939
1.46E+08	1	235.7
8.53E-09	1	2.07E-06
1.66E-16	1	2.89E-10

The mathematical models obtained from regression for each relation were shown in Table 9. For each regression, it was chosen the equation that had the less error in the prediction. Generally for functions which include the operation temperature, the regression had a high error as shown in Table 10. While for regressions with flow, the equation of a straight line satisfies the prediction. The Sum of Squares due to Error (SSE) for the equations in which the operation temperature was involved had a big value, however, as shown in Fig. 3, the maximum error for each data was equivalent to minus of 0.1% of the measure.

Obtaining these kind of correlations, it was possible decrease the complexity in the model of the reactor in order to facilitate the control and support the calculus involved in the behavior prediction of the oxidation reactor.

CONCLUSION

The physicochemical properties of each compound from the inlets streams were obtained from the literature and subsequently a correlation to the temperature and pressure worked at the oxidation reactor was made. In order to obtain all the characteristics for the reactor an energy and mass balance were made. The inlet stream to treat was obtained from the residues of an atmospheric fractionated distillation column for crude oil. The principal components of this stream were carbon chains and metals. For each group of component, a procedure was made to determine the energy generate by the oxidation of each component. It was obtained the main characteristics of design for an oxidation reactor which ensure a full combustion of the inlet stream. Furthermore, it was found the correlations between the main variables for which an error between the prediction and the real value were less of 0.1%.

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REFERENCES

01. Hou, P.Y., 2010. Oxidation of Metals and Alloys. Shreirs Corros., 1: 195-239.
02. Whitten, K.W. and R.E. Davis, 2008. Quimica/Chemistry. 1st Edn., Cengage Learning, Boston, Massachusetts, USA., ISBN-13:978-9706867988, Pages: 1176.
03. Brown, T.L., 2008. Chemistry: The Central Science. 11th Edn., Prentice Hall, Englewood Cliffs, NJ., USA., ISBN-13: 9780136002864.
04. Young, D.J., 2016. Oxidation of Pure Metals. In: High Temperature Oxidation and Corrosion of Metals, Young, D.J. (Ed.). Elsevier Ltd, Amsterdam, Netherlands, ISBN:978-0-08-100101-1, pp: 85-144.
05. Boateng, A.A., 2016. Combustion and Flame. In: Rotary Kilns: Transport Phenomena and Transport Processes, Boateng, A.A. (Ed.). Butterworth-Heinemann, Oxford, UK., ISBN:9780128038536, pp: 107-143.
06. Sarkar, D.K., 2015. Fuels and Combustion. In: Thermal Power Plant: Design and Operation, Sarkar, D.K. (Ed.). Elsevier, Amsterdam, Netherlands, ISBN:9780128017555, pp: 91-137.
07. Pacini-Petitjean, C., P. Faure, V. Burkle-Vitzthum, A. Randi and J. Pironon, 2015. Oxidation of N-hexadecane and crude oil in response to injection of a CO2/O2 mixture under depleted reservoir conditions: Experimental and kinetic modeling preliminary results. Intl. J. Greenhouse Gas Control., 35: 110-119.
08. Savelieva, V.A., N.S. Titova and A.M. Starik, 2017. Modeling study of Hydrogen production via partial oxidation of H2S-H2O blend. Intl. J. Hydrogen Energy, 42: 10854-10866.
09. Cengel, Y.A., and M.A. Boles, 2006. Thermodynamics: An Engineering Approach. 5th Edn., McGraw-Hill, New York.
10. Smith, J.M., H.C. Van Ness and M. M. Abbott, 2007. [Introduction to Thermodynamics and Heat Transfer]. McGrawHill, New York, USA., (In Spanish).
11. Spencer, H.M., 1948. Empirical heat capacity equations of gases and Graphite. Ind. Eng. Chem., 40: 2152-2154.
12. Kelley, K.K., 1960. High-temperature heat-content, heat-capacity and entropy data for the elements and inorganic compounds. US Bur. Mines Bull., Vol. 584,
13. Jones, D.S.J. and P.R. Pujado, 2006. Handbook of Petroleum Processing. Springer, New York, ISBN: 9781402028205, Pages: 1367.