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ARTICLE

Addition of carbon tetrachloride as propulsion to the thermal cracking reactor based on the amount of coke formed in different coil outlet temperatures (COT)

1

Afshin Davarpanah

Full Length Research Paper

Addition of carbon tetrachloride as propulsion to the thermal cracking reactor based on the amount of coke formed in different coil outlet temperatures (COT)

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Nowadays, polyvinyl chloride (PVC) is the most usual plastic. Therefore, to make PVC, its monomer called vinyl chloride (VCM) must be produced first. It is a severely endothermic reaction that is done in an ethylene dichloride thermal cracking reactor within a temperature range of 680 to 758°K and pressure range of 2500000 Pascal. Thus, this cracking reaction changes into hydrochloric acid and VCM. In production unit, monomeric chloride has the main and principal role as the core of the process of thermal cracking that occurs in the furnace. Increased wall temperature causes boil gas mixture and pyrolysis reactions. Regarding simulation, the results showed that the number of pyrolysis produced composition with maximum concentration in the length of the reactor. This illustrated that these compositions participated in secondary reactions. Furthermore, by increasing the amount of coil outlet temperatures, the amount of formed coke will increase. If carbon tetrachloride is considered as the chlorine radicals, it has an important role as the motivator in the cracking procedures, radicals causing an enhancement in VCM production.

Key words: Carbon tetrachloride, conversion factor, coke, coil outlet temperatures, thermal cracking.

INTRODUCTION

Designing and simulation of thermal cracking reactor of the chemical reactions in the processes and heat transfer in the furnace are very complex. Therefore, this process from the chemical reactions engineering perspective and from the perspective of transfer phenomena is highly regarded. Computational Fluid Dynamics (CFD) tools help us to investigate the development of detailed models of these reactors, and by understanding the basic principles, the optimized design of reactor, saving of cost and time performance of this equipment in a virtual

laboratory can be done. In this research, the author investigates the proposed model of 1,2-dichloroethane (EDC) cracking process in an industrial furnace and by operational data from a petrochemical unit, qualifies the model and removes its reductions. To begin, previous research done on this specific subject was studied. Moreover, the reactor mathematical models were provided and solved by numerical software. Thereby, the operation of the reactor at different operating conditions was investigated as well as sensitivity analysis of

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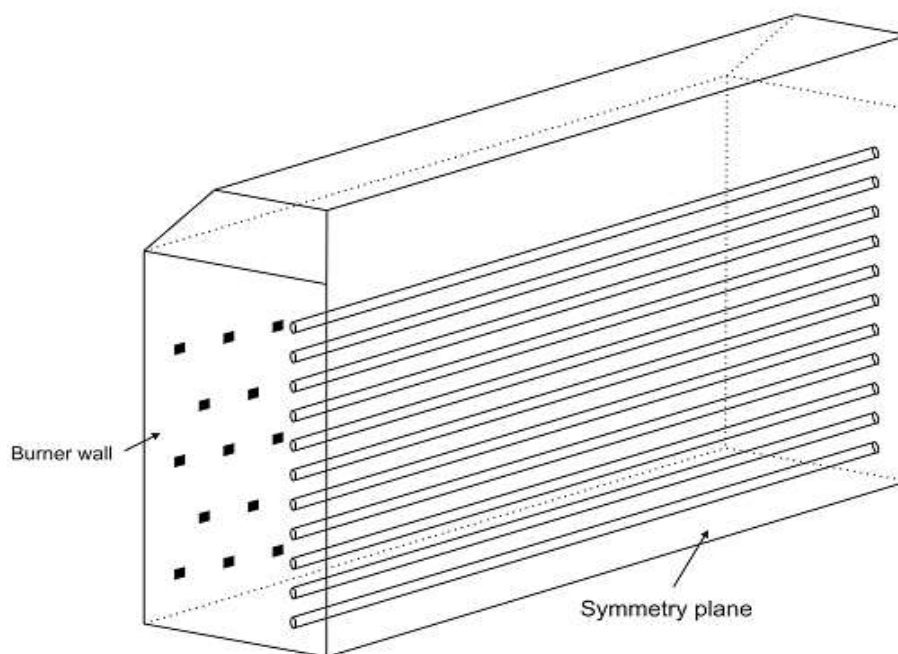


Figure 1. Placement of coil in the furnace.

effective parameters. As a result, new reactors or increasing the optimization capacity of existing reactors can be designed.

Molecular cracking

Molecular cracking is a process that is used in the petrochemical industry and is used to reduce their hydrocarbons molecular weight by breaking their bonds. This process is the main principal of converting crude oil to useful fuels such as gasoline, diesel, jet fuel and kerosene. Thermal cracking, catalyst cracking, hydrocracking and cracking by water vapour are the most useful cracking processes in the industry. This process is either done with high temperature and pressure without a catalyzer or with low temperature and pressure with a catalyzer.

Geometry of thermal cracking reactor

In EDC thermal cracking process, coils containing process fluid in a box called furnace, are positioned horizontally. Coils placed inside the furnace are shown in Figure 1 (Kaggerud, 2007). They are positioned on both sides of the furnace wall. By burning the gases of these furnaces heat is produced and then transferred to the coils by convection or radiation. The number of intended coils to simulate 11 rows of pipes (Inconel 600) with overall length of 95 m and length of each row tube is 13.5 m. The inner diameter of coils is 0.134 m and the distance between the centers of the two tubes is 0.32 m.

Schematic of one row of the coil in the software is in Figure 2. Furthermore, prospective a row of coil was shown in Figure 3.

Mass balance equation in the software is proposed in form of Equation.1

$$\frac{\partial(\rho y_i)}{\partial t} + \frac{\partial(\rho u_i y_i)}{\partial x_i} = -\frac{\partial J_i}{\partial x_i} + R_i + S_i \quad (1)$$

ρ is the density, t is the time, u_i is the potential energy, J_i is the diffusion term, S_i is the heat at point i , R_i is the input heat to the reactor.

Phrase J_i reflects the term infiltration, which is not used in this simulation (ANSYS, 2011). The energy equation in the Fluent software is as follows:

$$\frac{\partial}{\partial t}(\rho E) + \frac{\partial}{\partial x_i}(u_i(\rho E + p)) = \frac{\partial}{\partial x_i} \left(K_{eff} \frac{\partial T}{\partial x_i} - \sum_j h_j J_j + u_j(\tau_{ij})_{eff} \right) + S_h \quad (2)$$

ρ is the density, p is pressure, t is time, T is temperature, u_i is input potential energy, u_j is output potential energy, τ_{ij} is torque, J_j is output diffusion term, S_i is input thermal of chemical reactions, and S_h is

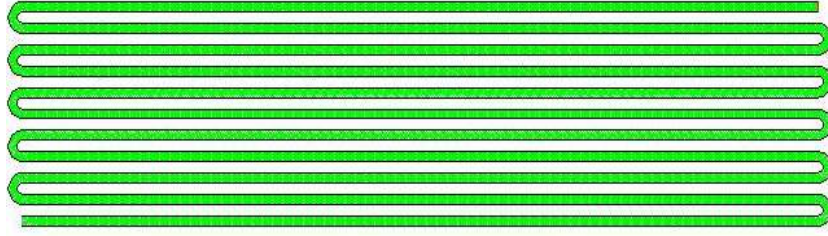


Figure 2. Schematic of one row of the coil in the software.



Figure 3. Prospective a row of coil.

thermal of chemical reactions, K_{eff} is the effective conductivity, and E is the total energy.

$K_t + K = K_{eff}$ is the effective conductivity, K_t turbulent thermal conductivity, according to the model used is the perturbation. The first three terms on the right side of the equation are an expression of directed energy transfer, distribution of components and dispersion of viscosity. The volume of EDC thermal cracking Energy reaction are being calculated in Table 1 (Chaochun et al., 2013). S_h is the thermal of chemical reactions (Berreni and Wang, 2011; Fogler, 1999; Bird et al., 2007). E is expressed as follows:

$$E = h - \frac{p}{\rho} + \frac{u_i^2}{2} \quad (3)$$

where u_i is the input potential energy, p is pressure, ρ is density, E is total energy, u_i is input potential energy, and h is the input heat.

Mass continuity equation in FLUENT software is in Equation 4:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0 \quad (4)$$

The aforementioned equation is the general form of the mass balance equation for compressible and non-compressible flows.

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial(\rho u_i u_j)}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} + \rho g_i + F_i \quad (5)$$

In the aforementioned equation, P is the static pressure, τ_{ij} is the tensor stress, ρg_i and F_i are physical forces of gravity and physical external factors in i direction. Tensor stress is as follows:

$$\tau_{ij} = \left[\mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \right] - \frac{2}{3} \mu \frac{\partial u_i}{\partial x_i} \delta_{ij} \quad (6)$$

where μ is the molecular viscosity and the second semester is the influence of volumetric expansion (ANSYS, 2011).

Standard k- ϵ model

This is a comprehensive model that accounts for the simplest turbulence model. Two educational turbulent models enable solving of the two transfer equations that separately determine turbulent length and time scale. Standard k- ϵ model is useful for powerful engineering calculations. The power of this equation, its economical and acceptable accuracy for a wide range of turbulent flow is as a result of its popularity in industrial flow and heat transfer simulation. This model is a semi-empirical model. Standard k- ϵ model is a model based on transfer equations for kinetic turbulent energy and dissipation rate (ϵ). In achieving the standard k- ϵ model it is assumed that the fully turbulent flow and molecular viscosity effects are ignored. Because of the strengths and weaknesses of the equation to improve its performance, k- ϵ realizable and k- ϵ RNG model were introduced. K and ϵ are obtained by solving simultaneously the following two equations:

$$\frac{\partial}{\partial t}(\rho K) + \frac{\partial}{\partial x_i}(\rho K v_i) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + G_k + G_b - \rho \epsilon - Y_M + S_K \quad (7)$$

Table 1. Energy of EDC thermal cracking reaction.

Reactions	A [(cm ³ /mole)n ⁻¹ s ⁻¹]	n	E (kJ/mole)
Radical reaction chain initialization			
EDC → R1 + R2	5.9 × 10 ¹⁵	1	342
CCl ₄ → R1 + R8	2.2 × 10 ¹²	1	230
Radical reaction chain propagation			
EDC + R1 → HCl + R3	1.3 × 10 ¹³	2	7
EDC + R5 → VCM + R3	1.2 × 10 ¹³	2	34
EDC + R2 → EC + R3	1.0 × 10 ¹²	2	42
EDC + R4 → 1,1 + R3	5.0 × 10 ¹¹	2	45
EDC + R6 → 1,1,2 + R3	2.0 × 10 ¹¹	2	48
EDC + R7 → 1,1,1,2 + R3	1.0 × 10 ¹¹	2	56
EDC + R8 → CHCl ₃ + R3	1.0 × 10 ¹²	2	63
VCM + R1 → R4	9.1 × 10 ¹⁰	2	0
VCM + R1 → HCl + R5	1.2 × 10 ¹⁴	2	56
VCM + R5 → CP + R1	5.0 × 10 ¹¹	2	31
VCM + R4 → C ₄ H ₆ H ₂ + R1	2.0 × 10 ¹⁰	2	30
VCM + R2 → EC + R5	3.0 × 10 ¹¹	2	61
R3 ↔ VCM + R1	2.1 × 10 ¹⁴	1	84
R5 ↔ C ₂ H ₂ + R1	5.0 × 10 ¹⁴	1	90
R6 ↔ Di + R1	2.0 × 10 ¹³	1	70
R7 ↔ Tri + R1	2.5 × 10 ¹³	1	70
2C ₂ H ₂ + R5 → C ₆ H ₆ + R1	1.0 × 10 ¹⁴	2	20
EC + R1 → HCl + R2	1.7 × 10 ¹³	1	4
1,1 + R1 → HCl + R4	1.2 × 10 ¹³	1	6
1,1,2 + R1 → HCl + R6	1.7 × 10 ¹³	1	15
1,1,1,2 + R1 → HCl + R7	1.7 × 10 ¹³	2	17
CHCl ₃ + R1 → HCl + R8	1.6 × 10 ¹³	2	14
CCl ₄ + R5 → Di + R8	5.0 × 10 ¹¹	2	33
CCl ₄ + R4 → 1,1,2 + R8	1.0 × 10 ¹²	2	33
CCl ₄ + R5 → 1,1,1,2 + R8	5.0 × 10 ¹¹	2	33
Radical reaction chain termination			
R2 + R1 → VCM + HCl	1.0 × 10 ¹³	2	13
R3 + R1 → Di + HCl	1.0 × 10 ¹³	2	12
R6 + R8 → Di + CCl ₄	1.0 × 10 ¹³	2	13
C ₂ H ₂ + 2R1 → 2C + 2HCl	1.6 × 10 ¹⁴	2	70

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \frac{\partial}{\partial x_i}(\rho\varepsilon v_i) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] + C_{1\varepsilon} G_k \frac{\varepsilon}{k} - C_{2\varepsilon} \rho \frac{\varepsilon^2}{k} + S_\varepsilon \quad (8)$$

G_k is the turbulent kinetic energy generated due to the gradient of speed, G_b is the turbulent kinetic energy generated due to the buoyancy forces, Y_M is the Share Swinging delay in the compressibility turbulence for a total loss of (j), $C_{1\varepsilon}$ is the constant parameter of model = 1.44, $C_{2\varepsilon}$ = 1.92, σ_k is the turbulent Prantel numbers for $k = 1$, σ_ε is the turbulent Prantel number for $\varepsilon = 1.3$, S_K is the term defined source for k, S_ε is the term defining

source for ε , and μ_t is the turbulence viscosity that can be obtained from the following equation:

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon} \quad (9)$$

RNG k- ε model

This model is based on statistical methods. This model is the same as the standard k- ε model, but with the following modifications:

(1) An additional term (ε) that significantly increases

Table 2. Thermo-physical properties of coils.

Temperature (°K)	Transfer coefficient (W/m.K)
373	15.9
573	21.2
753	25.7
973	25.7
Density (kg/m ³)	8470
Heat capacity (j/kg.k)	444

accuracy for flow to layer velocity.

(2) The effect of the rotational movement (vortex motion) included turbulences and increases accuracy for rotary flow.

(3) An analytical formula for turbulent Prantel numbers is provided, as standard k-ε model is considered a fixed amount

(4) While the standard k-ε model is the model for high Reynolds numbers, the theory of RNG for analysis of a differential equation for the turbulent viscosity can be provided considering the effects of low Reynolds. Effective use of this feature depends on proper behavior of the region near the wall of the furnace.

K-ε realizable model

This model has limitations on Reynolds stresses that match with the physics of turbulent flows. This is possibly not in the standard k-ε model and not in the k-ε RNG model; but in places with a large curvature in flow lines, vortex and rotation of the screw. K-ε RNG and k-ε realizable models have significant progress towards standard k-ε model. Preliminary studies show that the k-ε realizable model between k-ε models has best performance for confirmation numbers of complex flows and segregated flows. In all of these cases, the performance of this model is better than the standard k-ε model. As it was observed that in the standard k-ε model, turbulent viscosity achieved the following equation:

$$\mu_t = \rho C_\mu \frac{K^2}{\varepsilon} \quad (10)$$

That C_μ is constant, but in the k-ε realizable C_μ is achieved by the following equation:

$$C_\mu = \frac{1}{A_o + A_s \frac{KU^*}{\varepsilon}} \quad (11)$$

$$U^* \equiv \sqrt{S_j S_j + \bar{\Omega}_j \bar{\Omega}_j} \quad (12)$$

$$\bar{\Omega}_j = \Omega_j - 2\varepsilon_{jk} \omega_k \quad (13)$$

$$\Omega_j = \bar{\Omega}_j - \varepsilon_{jk} \omega_k \quad (14)$$

$\bar{\Omega}_j$ Average rate of tensor with rotational speed is ω_k ;

constants are defined as follows:

$$A_o = 4/04, A_s = \sqrt{6} \cos \emptyset$$

$$\emptyset = \frac{1}{3} \cos^{-1} \left(\frac{\sqrt{6} S_j S_{jk} S_{ki}}{(S_j S_j)^{3/2}} \right) \quad (15)$$

$$S_j = \frac{1}{2} \left(\frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) \quad (16)$$

As seen, C_μ placed a function of the average strain, rotational speeds, the angle speed of rotation systems, and turbulent fields which are k and ε.

Thermo-physical properties of coils are being illustrated in Table 2.

Wall of furnace

The profile of heat is applied in the walls. A total of eleven walls were located and each row of coil has a heat profile of its own. The thermal flux resulting from furnaces applied on the coils level used for proposed profiles was provided by Kegard (2007). The length of each row of coils can be categorized as profile provided by the amount of heat to be entered in the software (figure 4).

METHODOLOGY OF THE WORK (SIMULATION)

Boundary conditions of cracking reactor

Inlet flow

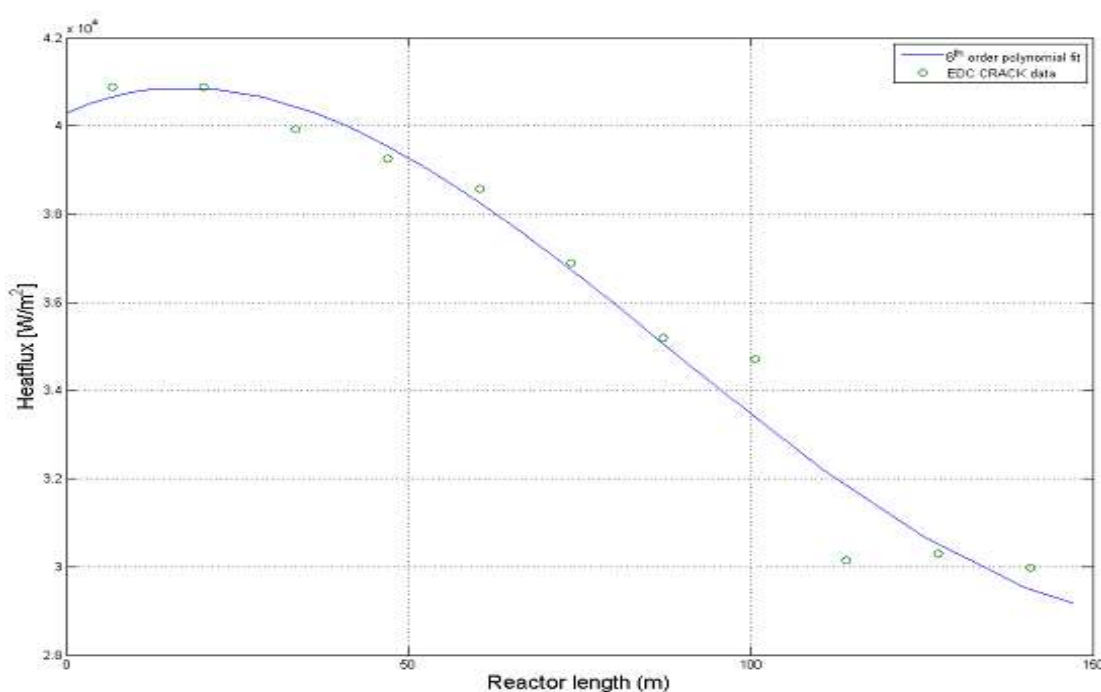
Input for fluid flow based on mass flow rate and percentage of each of the compounds at the entrance of the inlet is used for the mass

Table 3. Input fluid conditions

Feed mass flow rate	6.086 kg/s
Mass percentage of input EDC	0.9707
Mass percentage of input VCM	0.0184
Mass percentage of HCL input	0.0109

Table 4. Applied boundary conditions in the software.

Location	Type of boundary condition
Walls	Heat flux
Input gas	Input mass rate
Output flow rate	Output pressure

**Figure 4.** Thermal profiles calculated by Kegard.

flow condition that accounts for the boundary condition (Table 3).

Output flow

The output flow is used for pressure boundary condition. The boundary conditions are summarized in Table 4. The conversion factor and amount of coke formed are based on different COTs.

In this part of the research, the different COTs EDC conversion factor and the amount of formed coke are investigated. The amounts of COT based on recent issues in review of EDC cracking processes with values of 760, 770, 780 and 790 are selected. To achieve this profile, it is first calculated $\frac{COT_{desired}}{COT_{base}}$ and by using

the proportion, a variable factor is described. As a result, the new temperature profile in a particular COT from the new data was achieved. In this method, input temperature of the coil does not change and base COT temperature multiplies in the $\frac{COT_{desired}}{COT_{base}}$; the

other base profile in Equations 17 and 18 multiplies in a constant parameter to obtain new profile points.

$$Weight\ factor(x) = \frac{Temperature(x) - Temperature(l=0)}{Temperature(l=150) - Temperature(l=0)} \quad (17)$$

$$T(x) = Weight\ factor(x) \times \frac{T(l=150)_{desired}}{774.1} \times T_{base} \quad (18)$$

The results of these calculations can be seen in Figure 5. COT

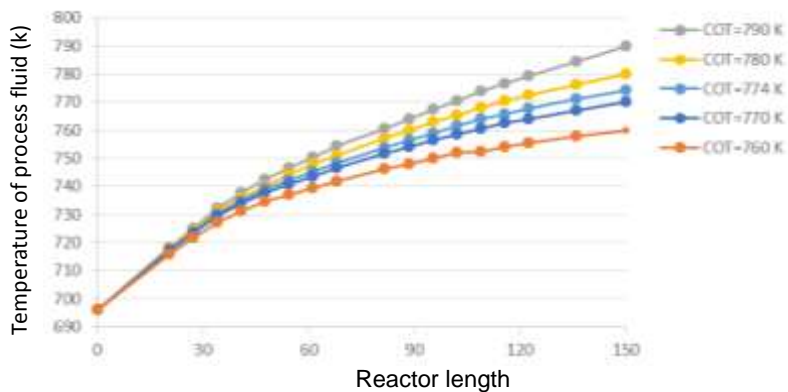


Figure 5. Process fluid temperature profile along the reactor.

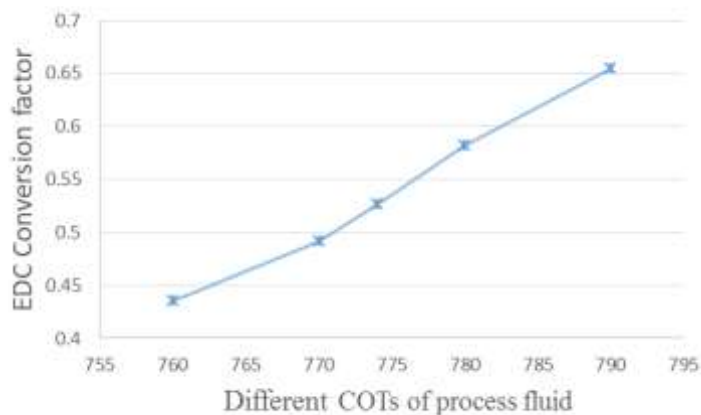


Figure 6. Process fluid temperature profile along the reactor.

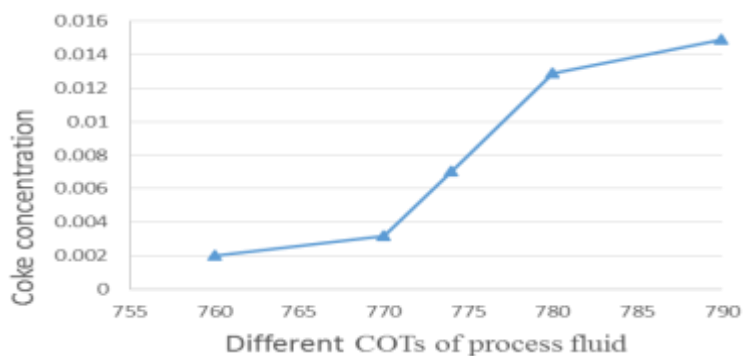


Figure 7. Process fluid temperature profile along the reactor.

different temperature profiles were obtained. Figure 6 indicates the EDC conversion factor in different COTs; higher conversion factor will be higher in the COTs. In Figure 7, if the amount of COT is higher, the amount of formed coke also will be higher. So by regarding the simulation results, it can be said that for optimum economic performance of furnace, the temperature profile of the fluid is very important.

INVESTIGATING ADDING CARBON TETRACHLORIDE AS PROPULSION

By adding this compound to the feed in addition to increased conversion factor, it has other effects on the process. Due to increasing number of chlorine radicals in

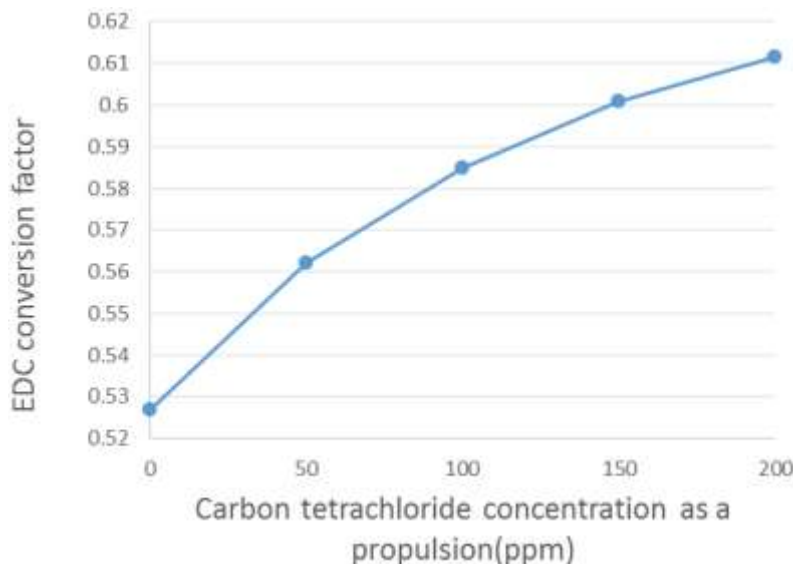


Figure 8. Conversion percentage change Ay.dy.sy in different concentrations of carbon tetrachloride.

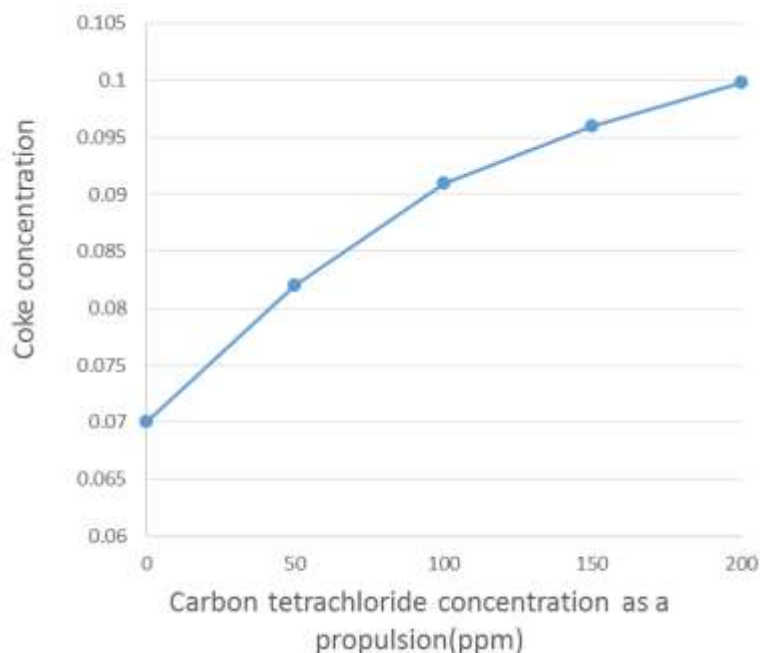


Figure 9. Change the concentration of coke in different concentrations of carbon tetrachloride.

the process, the number of unwanted compounds and acetylene production, coke production increased. Creating unwanted compounds in the next stages, in addition to VCM treating problem leads to an important loss. As shown in Figure 8, conversion factor increases with increasing carbon tetrachloride; on the other hand, in Figure 9, coke is formed with increase in carbon tetrachloride. Regarding simulation results, it can be said

that for optimum economic performance of furnace, the temperature profile of the fluid is very important. Therefore, by optimizing the amount of carbon tetrachloride added to the feed for economic performance of thermal cracking unit is very important. In this amount of propulsion conversion factor increases as an allowable limit and reactor performance for forming coke and unwanted compounds are economical (Figure 5).

Conclusion

K- ϵ realizable model is the most appropriate model for calculation because of the following reasons (Berreni and Wang, 2011):

- (1) This version contains a new formula for turbulence viscosity.
- (2) A modified transferring equation for scattering rate, ϵ , can be considered. Therefore, this model is an exact equation for fluctuations transfer.


In this research, the effect of adding carbon tetrachloride as a propulsion has been investigated. According to the result of this research and other issues, if the amount of this compound is not more than 100 ppm, conversion factor will be increased; if this amount is more than 100 ppm, it is not suggested economically.

Conflict of Interests

The authors have not declared any conflict of interests.

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