Mathematical Model for Coking Fouling in Distillation Units

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Abstract:

Fouling thickness progress can be predicted by mathematical models when dealing with thermal equipments where previous calibration can be easily obtained. In case of heat exchangersthis calibration is obtained by evaluating temperature and mass flux that result in a specific thermal resistance. However, some other process equipments used in oil industry like distillation columns and reactors do not allow such required calibration

parameters. Thiswork presents anew mathematical modelto predict the growthofcokefoulingspecifically for these types of equipments when working at sufficiently high temperatures to produce internal thermal cracking and consequently, coke fouling. This model is based on thermal cracking chemical analysis but also considers the bursting effects of the fluid turbulence as a probabilistic mitigation factor. The first simulated application was done on a distributor of a heavy gasoil section of a vacuum distillation unit. The obtained results are presented in a graphical form showing the effect of various parameters such as temperature and fluid velocity on the coke fouling growth rate. The flow initial evaluationsshowed promising results, but additional testswould be neededtofurther validate the model effectiveness

Keywords: Coke, Thermal cracking, Fouling, Mathematical model.

1. Introduction:

The first fouling prediction models emerged in a generic form and they do not include any specific mechanisms for the fouling process. They relate the fouling rate of change in function of time only. The first model was suggested by Kern and Seaton [2],which was based on the hypothesis of the existence of two independent processes, namely: deposition and removal, both depend on the shear stress provoked by the flow, followed by the models of Konak[3] and Epstein [4].

Recently, the basic fouling models have turned out to be less common, since each individual mechanism of fouling demands a specific model. Therefore, the phenomena of deposition and removal are difficult to be predicted simultaneously. According to Taborek et al. [5], this fact can be understood under two point views: removal of already deposited

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materials or suppression of the deposition mechanism. Both of the deposition and removal processes or even the suppression of the deposition process are complex physic-chemical phenomena.

A good revision of the main existing mathematical models of the fouling phenomenon permits better correlation of the characteristics of each one and determines the more adequate for each specific situation, for the preheating or even for the distillation steps. Besides the basic models, a classification of the main models specific for fouling caused by chemical reactions can be found in Bott[6], which contains details and restrictions of application.

Mechanicist mathematical models are based on four deposition mechanisms: chemical reaction, mass transfer, mass sedimentation and evaporation. The four mechanisms can occur simultaneously, but in the major part of the coke fouling models, only the first two can be considered to occur in two or three steps[5]. Thus, the most models describe the fouling by difference between two terms: a term that takes in consideration the involved physic-chemical reactions and another that takes into account the fluid hydrodynamic.

Among the simpler mechanicist mathematical models is Fernandez-Baujin[7] which is developed from a material balance that consider all reactant precursors that enter the control volume by mass transfer and suffer reaction generating the fouling agent. The control volume is assumed to be the film formed on the fouled wall. The model results in the differential expression and its application is limited to plane surfaces, but it can be considered as one of the fundamental mechanical models, from which the others were derived. This model depends on a diffusion process and on a chemical reaction. The slower would define the fouling velocity.

The diffusion can be neglected if the diffusion constant was very high in comparison to chemical reaction. The same reasoning also applies to the chemical reaction. The estimation of the diffusion phenomenon is a complex task. The limitation can be overcome by substituting the diffusion by a probability parameter, P, transforming the expression of Fernandez-Baujin [7]as it was done by Paterson e Fryer [8]. Associating the diffusion of adhesion to the flow conditions, Paterson and Fryer [8] showed that fouling is inversely proportional to the mean flow velocity.

Crittenden and Kolaczkowski[9] also have improved the model of Fernandez-Baujin[7]. They included the fouling agent convection back to the fluid medium by introducing the part relative to the removal phenomenon. The diffusion in the removal process was admitted to be independent of deposition and that the fouling agent concentration in the fluid medium was nil.

Another model was suggested by Takatsuka et al. [10], specifically for coke fouling due to petroleum cracking in furnaces. It was observed that in different types of furnaces, the coking rate depends on temperature, pressure, fluid velocity and processed oil properties. The effect of all of these variables can be foreseen, using this model, along the whole piping length. The fouling products are adhered to the pipes internal walls causing a reduction in the internal diameter.

The coking rate results in a series of complex phenomenon, but it can be assumed in a simplified form as being proportional to the cracking of a hypothetical component present in the fluid concentration. The deposition rate is explicit through a material balance between two diffusing processes and a process of cracking chemical reaction where the reactants are exclusively of the soluble in n-heptane type (maltenes). The insoluble

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products in n-heptane (asfaltenes) were observed, but they were considered to be of a negligible order.

Besides the complexity, the model of Takatsuka et al. [10] was criticized by Wiehe[11], who demonstrated that both maltenes and asfaltenes suffer decomposition and showed that the chemical mechanism adopted by Takatsuka et al. [10] does not agree with the experimental results.

Briefly, the major part of the existing models is derived, with small modifications, from the model of Crittenden e Kolaczkowski[9], attributing the physical meaning to the constants of deposition and removal. The model of Polley et al. [12] ranks among the most recent and consistent of refinements applied to the model of Ebert e Panchal [13]. Theoretically, all these mathematical models can be used to predict the fouling in well calibrated oil processing equipments. That is easily done in heater exchanges, but not so simple when occurs in the interior of large equipment like reactors and distillation columns.

This work overcomes the above mentioned lack of information by suggesting an alternative model based on the amount of coke obtained at very high temperature which is taken as a condition limit in which all fluid volume reacts completely to produce coke and volatiles. The action of turbulence bursting effect is taken as a mitigation factor. The main aim of this work is to solve an estimation of the fouling growth in internal pipes of oil process distillation units. The fouling is commonly found as coke type that comes from thermal decomposition of the petroleum heavy fractions and cause economical and environmental problems of significant impact[1].

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2. Mathematical Modeling:

The complexity of the mathematical modeling is reduced by adopting the following simplifications:

- The model is applicable to heavy hydrocarbon fluids that present thermal cracking when submitted to high temperatures;
- The coke is originated in the entire fluid when heated into high temperatures, but fouling occurs by chemical reaction only at the wall-fluid interface. As the fouling layer grows, the interface reaction moves up creating a fresh coke and increasingthe top of the fouling layer and turning the deeper layers slowly into hard coke;
- The reaction volume would be determined throughout the • analyses of the velocity profile of the flow, establish the point where the velocity of the fluid implies a residence time greater than the time necessary to complete the conversion of the hydrocarbon material coke and volatiles. As to а simplification, the film thickness to be considered corresponds to the viscous sub layer which is a function of the fluid flow Reynolds number. Above this point, the fluid has high velocity and there is no sufficient time to complete the thermal reaction to produce adherent materials. But, if occurs, the carbon particulates produced will remain immersed in the fluid and will be carried out. Within the viscous layer, it is assumed that the fluid has a low velocity and therefore, it has enough time to start thermal reaction producing adherent solids that increase its own resident time.
- Due to the low velocity, the viscous sub-layer is assumed to be a batch closed thin thermal reactor where the whole fluid is

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converted by cracking into two fractions: paraffin oil and solid coke. The oil is slowly carried out by the fluid and the solid coke remains as fresh coke fouling. As the time goes on, the fouling layer grows as a result of this deposition. The cracking reaction is governed by a first order kinetics, and the time needed to be completed is given by

$$k.t = k_{lim}.t_{lim} \tag{1}$$

The chemical constant rate, *k*, is a temperature dependent that varies according to the Arrhenius Equation. In Eq. (1) k_{lim} represents the value for this constant at high temperature (~550 °C) when the thermal decomposition demands a time t_{lim} to crack all fluid in the reactor to basically only solid coke slightly covered by a thin film of heavy paraffin oil. The rest of the oil leaves the reaction as volatiles products. At this high temperature, the amount of obtained coke, α , represents the maximum quantity produced by the fluid by complete reaction. At others temperatures, the time for complete reaction is inversely proportional to the constant rate. This hypothesis admits the viscous sublayer to be the reactor which is only valid when the resident time of the fluid is much lower than the time for the complete conversion. Otherwise, the whole volume in the tube would be in reaction and this mathematical model turns out to be inadequate. By definition, the deposited fouling thickness at each period of time necessary to complete the reaction is calculated by

$$\Delta x_i = \frac{\Delta m_i}{A \cdot \rho_i} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot \frac{k}{k_{lim}} \cdot \frac{t}{t_{lim}}$$
(2)

where Δx is the fouling thickness increase, [m], developed at the time intervaldetermined by the quotient formed among t and t_{lim} ; ρ_f and ρ_i which

are the specific mass of the fluid and the fouling $[kg/m^3]$, respectively; *A* represents the base of the volume of the reactor $[m^2]$, in which *e* is its thickness [m], Δm_i is the amount of mass deposited on the area *A* [kg].For an infinitesimal time, the expression of Eq. (2) becomes

$$\frac{dx_i}{dt} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot \frac{k}{k_{lim} t_{lim}}$$
(3)

Applying the Arrenhius Law on both k and k_{lim} , we obtain

$$\frac{dx_i}{dt} = \alpha \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot K.\exp\left(-\frac{E}{R.T}\right)$$
(4)

where K is a constant $[s^{-1}]$, defined Eq. (5), with E as the activation energy for the cracking reaction, R is the deal gas constant and T is the absolute temperature at which the reaction occurs. The reciprocal of K is assumed as equal to the adhesion time at work temperature, i.e., the necessary time to rich the reaction's end with complete conversion of the fluid to volatiles and solid coke.

$$K = \frac{1}{t_{lim} \cdot \exp\left(-\frac{E}{R.T_{lim}}\right)}$$
(5)

The expression of Eq. (4) is valid for linear fouling growthdueconstant thickness e and temperature T. In the case of nofluid flow, the static fluid has no implications in the fouling increase and e is adopted as the thickness of the oil film of the internal surfaces.

If the fresh coke (porous coke) stay adherent on the fouling layer during the necessary time to reach the maturate state, it becomes solid (hard coke) as a real part of the fouling layer. During this time, the coke is tied to

the layer by weak forces that increase with time. If turbulent flow condition was considering, a probability factor,*P*, is necessary to express the fluid mitigation action while the coke maturates. As suggested by Vatistas[14] during the maturation time, the turbulent action of bursting effects of the fluid has great influence on the fouling mitigation of allun-maturated parts of the coke. Assuming total adherence when the material is completely reacted, and in this case the adherence time is given by

$$t_a = \frac{k_{lim} t_{lim}}{k} = \frac{1}{K} \exp\left(\frac{E}{R.T}\right)$$
(6)

The adherence is also a function of the fluid flow condition, and therefore, the quotient among the adherence time and the period between two burst events gives the dimensionless time t^* that provides the adhesion probability [14].

$$t^* = \frac{1}{K} \cdot \frac{\vartheta^2}{100.\nu} \exp\left(\frac{E}{R.T}\right) = \frac{\tau_w}{100.K.\mu} \exp\left(\frac{E}{R.T}\right)$$
(7)

In which ϑ is the wall-friction velocity [m/s] and ν is the kinetic viscosity $[m^2/s]$. With this Vatistas' probabilistic concept[14], the final form becomes

$$\frac{dx_i}{dt} = \alpha \cdot (1 - \beta)^{t^*} \cdot e \cdot \frac{\rho_f}{\rho_i} \cdot K \cdot \exp\left(-\frac{E}{R.T}\right)$$
(8)

In Eq. (8), *e* is the viscous sublayerthickness [m] and *K* is the timeconstant of reaction $[s^{-1}]$, correlates to the conversion at limit conditions. All other terms are dimensionless. α is the fraction of coke obtained at complete reaction of the hydrocarbon to coke and volatiles; β is a factor correlates the mitigation efficiency of the bursting effect action and t^* is the dimensionless time [14]. Both, the dimensionless time, t^* , and

the viscous sublayer thickness depend on the temperature and velocity of the fluid, which inturndepend on the diameterof thepipeand the fouling thickness.

Comparing with others, this model is similar to the model presented by Paterson and Fryer (1988). The two model differs only on the physical significance of α . When all parameters are considered to be constants the model becomes a basic one as in ESDU(Engineering Sciences Data Unit)[15]. The flow influence given by the viscous sublayer thickness and the probabilistic factor suggest by Vatistas[14]while Paterson and Fryer model [8] use the mean velocity of the fluid.

Theadvantage of the proposed model is the means adopted to implement the constant values to α , β and K. K and α are obtained via chemical analysis, and β is adjusted by hypothesis assuming that the generated coke is all deposited when there is no flow. Then β is attributed a value that makes an adhesion probability of 0.99 when the fluid velocity is minimal, about 0,1 m/s. This generate a value of $1,5 \times 10^{-7}$. As all other adifferential this is also presented as equation models. whosesolutionisobtained vianumerical integration of sequential time steps.

3. Numerical Solution:

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Considering a turbulent flow in a pipe with diameter *D* and a homogeneous distribution of the deposited coke on the pipe internal surfaces, the small amount deposited after each step modifies the pipe diameter and therefore changes the flow velocity, imposing new flow conditions for the next time interval. For a given heavy hydrocarbon sample, we can get via chemical analysis: α , the amount of coke produced by the oil when suffers thermal cracking; k_{lim} and t_{lim} , the values that define

the K constant, and finally the respective activation energy for the cracking reactions, E. The working temperature T determines the dynamic viscosity of the fluid. So, with a predetermined flow Q, the sequential steps of calculations are:

Step 1 - The mean flow velocity, by
$$u_f = \frac{4.Q}{\pi . D^2}$$
; (9)

Step 2 - The ReynoldsNumber, given by Re= $\frac{\rho_f . u_f . D}{\mu} = \frac{u_f . D}{v}$; (10)

Step 3 - The friction factor f, normally calculated with the transcendental Colebrook equation, with a complicated solution. In this case, a first value obtained by Miller equation Eq. (11), which presents a deviation of about 10%, giving satisfactory result for initial evaluations [16];

$$f = 0,25 \left[\log \left(\frac{\sigma/D}{3,7} + \frac{5,74}{\text{Re}^{0.9}} \right) \right]^{-2}$$
(11)

Step 4 - The shear stress τ_w , is a function of the fluid nature and the flow profile, as shownby Eq.(12). In this case, for simulation purposes only, it is approximated by Eq.(13), attributed to Asomaning et al [17];

$$\tau_{w} = \mu \frac{d(u_{f})}{dy}$$
(12)
$$\tau_{w} = \left(\frac{f}{2}\right) \rho . u_{f}^{2}$$
(13)

Step 5 - The viscous sublayer e, is calculated by Eq. (14) attributed to Kay andNedderman(18);

$$e = \frac{5\mu}{\sqrt{\rho_f \, \tau_w}} \tag{14}$$

Step 6 - The wall-friction velocity ϑ , given byEq. (15):

$$\vartheta = \sqrt{\frac{\tau_w}{\rho_f}} \tag{15}$$

Step 7 - The dimensionless time is given by Eq. (7)

Step 8 - And finally, the fouling increment Δx_i is calculated by Eq. (8). As the thickness increasing reduces the effective flow diameter imposing new conditions to the flow.Then, the new conditions are iteratively recalculated by returning to step 1.

3.1 Model Validation:

This mathematical model was applied to simulate the fouling process in an internal pipe of oil distributor, Fig. 1, located at a vacuum oil distillation column with a heavy gasoil as a fluid, working normally at $385^{\circ}C$. By simplification, the quotient among the specific mass of fluid about to $790kg/m^3$ and the coke that vary from 670 to $930kg/m^3$ [19]was unconsidered by resulting in a factor close to one. The fouling deep in this distributor was evaluated by a qualitative and visual scraping at some and random points.

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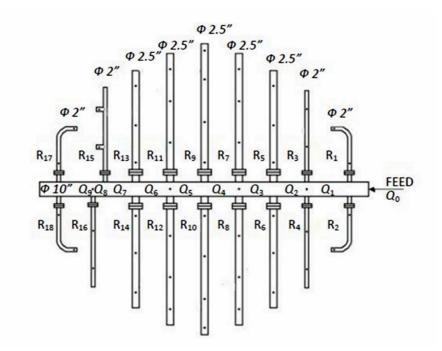


Figure 1 -Heavy gasoil distributor of a vacuum distillation unit.

The numerical integration for all simulations was done in EXCELTM(2007) for a campaign period of 6 years (2192 days). This period is used because the refinery takes out the pipes for maintenance each 6 years. As the fouling in oil process is a long period phenomenon, the time step was considered as a day. All necessary known data is shown in Table 1.

The activation energy of 137kJ/mol, the Arrenhius linear constant k_0 equal to $514803s^{-1}$ and the amount of coke at limit conditions, α , of 25% over the oil mass sampled was established by chemical analysis. The energy activation was coherent to other authors ([20], [21],[22],[23]). Although these experimental results needbetter valuation by making

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alargernumberoftests, the values here applied are reasonable to be applied as a simulation example.

The wall roughness was considered as 0,1mm, as normally applied to stainless steel pipes. All simulations took into account the mean fluid velocities to be 0,1m/s, 0,25m/s, 0,5m/s, 1,0m/s, and 1,2m/s, complemented with further speeds of 0,01m/s and 1,5m/ as lower and upperlimits, respectively.

Variable	Value	Dimension
Activation energy, <i>E</i>	137	kJ / mol
Start pipe diameter, <i>D</i>	0,254	т
Wall roughness, σ	1×10 ⁻⁴	т
Viscosity,µ	1,14×10 ⁻³	Pa.s
Specific mass of oil, ρ_f	749	kg/m^3
Constant α	0,25	-
Constant β	1,5×10 ⁻⁷	-
Time reaction at limit condition, t_{lim}	2	Н
Constant rate at limit condition, k_{lim}	0,9836	h^{-1}
Ideal gas constant, R	8,314×10 ⁻³	kJ /(mol.K)

Table 1 –Input data for model validation.

4. Results and Discussion:

The conversion rate velocity is implieddirectly at the fouling layer growth even if the fluid is subjected to milder kinetics conditions. This produces the same results of complete reaction limit conditions, that is, sufficient time forthe reaction to be completed. At 550°C the complete

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conversion needsonly several minutes while at 385°C the same reaction requires 84 hours.

Fig. 2 presents the effect of the mean fluid velocity and temperature on the coke fouling thickness. As can be shown from the figure, the influence of fluid velocity on the fouling thickness growth is less evident for lower temperatures that permit to the fluid more mitigatedaction due to the longer adhesion time. All curves tend to get a minimal fouling thickness with velocity increase, and become negligible for different velocities depending on temperature. For example, the influence of velocity on the fouling thickness would be negligible after 1.2 m/s for temperatures below 390°C.

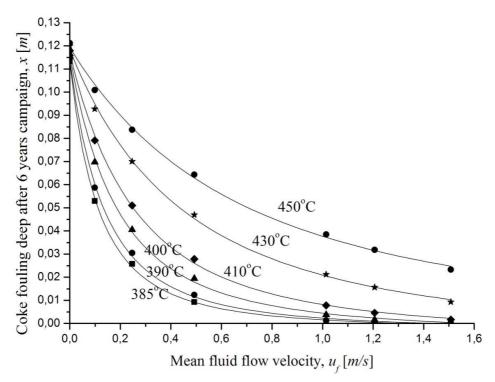
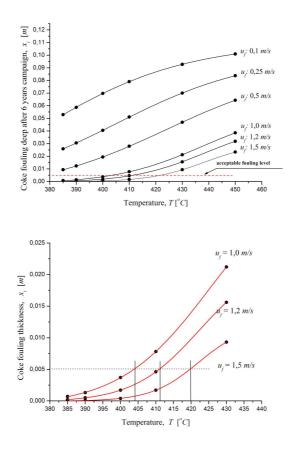


Figure 2–Fluid flow influence on the fouling thickness after a 6 years processing campaign.

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The fluid flow influence is more visible in Fig. 3 that correlates the fouling thickness with temperature. Assumingamaximumacceptablefoulingdefinedthroughadashed line as shown in the Figure, states the same fouling thickness to each fluid velocity, but that occurs to different temperatures. Approximately 405° C for 1m/s, 409° C for 1,2m/s and 424° C for 1,5m/s. The dashed line was purposely assumed as an exaggerated fouling of 0,5mm. For a better view, when we desire a less thick incrustation we can enlarge the graphic on Fig. 3a showing only the interesting parts as shown in Fig. 3b. The threshold condition to each flow case is determined when fouling approaches zero.



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Figure3–a) Temperature influence on the fouling thickness after a 6 years processing campaign; b) Enlargement of the graphic shown in Fig. 3a

As we can see from Fig. 3b, the horizontal line determines a temperature to each fluid velocity. Thus, this mathematical model also provides a way to establish the temperature of the cracking reaction start, knowing as *threshold condition*[13]. Analytically this point could be reached by making the mathematical expression of Eq. (8) equal to zero which can be solved to find correspondent temperature. However, this procedure is complicate and difficult, it is better be solved by association of allthe pointsobtained from the numerical threshold producing a new chart, Fig. 4. This chart suggests that any point below the curve of *5mm* is considered to be an acceptable fouling.

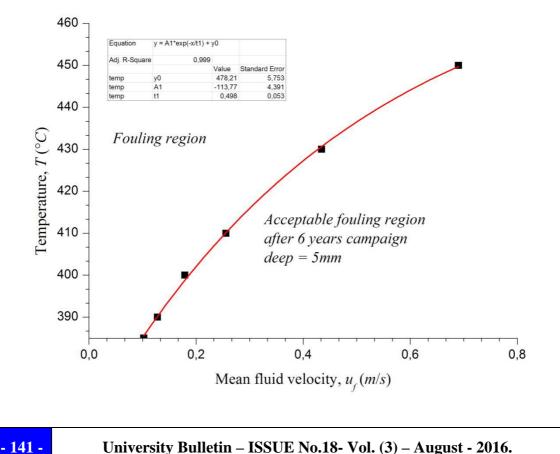


Figure4 – Dependence of fluid velocities and the temperatures of start cracking reactions.

As a validation procedure this model was applied to verify the the main distributor branch shown in the Fig. fouling in 1. assuming an inflow of $0.0754 \text{ m}^3/\text{s}$ and the reductionin the flow due todischarge after eachderived sectionextensionsin a ratio $of 0.00145 m^3/s$ for each existing sprinkler along secondary branches. The simulations also considered six years of operation time at 385° C providing the results of internal fouling thickness showninFig.5 thatshows an increase of fouling as the fluid flow decreases from the inlet (Q_1) to the final extremity (O_0) of the manifold. As we can see in this graphic the fouling thickness rise continuously at each branch reaching over 4 cm in the last branch.

In Fig. 1, point Q_0 corresponds to the entryof the fluid in the manifoldand point Q_9 istheopposite extreme,or the the closed end, where flows only the discharge of the last four sprinklers. Fouling of the orderof4*cm*, at point Q₉ is too close to the thickness qualitatively observed during the maintenance shutdown, both insize and position. At this stage the lastextensionof sprinklers were blockedbycokein just the thedistributorside,a total ofsevensprinklersfullyclosed.The foulingwas morepronouncedat thefinal stage because the distributor was simplified builtwithasinglediameterat every derivation when it shouldbe reduced ateach nodetomaintainanaveragespeedinorder of at least1.0m/s.The same way the model was applied to themain extension could be applied tothesidebranches.

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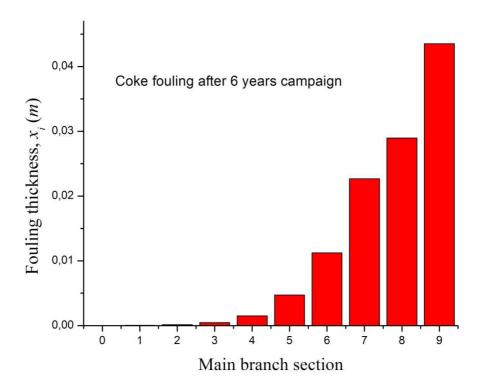


Figure5 – Calculated fouling depth after 6 years of processing campaign at the main branch manifold, shown in Fig. 1

5. Conclusions:

All mathematical models for fouling prediction have great similarities. Any of them can be applied in coke fouling prediction if its constants were well adjusted. The main factor that difficult the fouling prediction in distillation process is the lack of information about adjusting constants of the mathematical models at each particular situation. Techniques and methods that insure the obtainment of this data by precise experimental form do not exist. In part the high temperatures involved in the fouling process in the petroleum industry, difficult experimental processes. In case of fouling in heat exchangers this lack is less, because of

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the data can be obtained indirectly through the temperatures and the flow rates. With respect to the rest of the process equipments, the techniques knowledges are still insufficient. The model suggested in this work is an alternative to overcome the difficulties presented in the other models when used in distillation processes. The presented results in the real case showed satisfactory results compared with observed fouling in industrial scale equipments.

Although the resultswere madeina qualitative way justvisually evaluating the depthofinlay and the simulation resultswere consistent with the observation madein the distributor. In order to have an effective validation of the model, newsituations must be studied and tested.

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Nomenclature:

A	Superficial area $[m^2]$;
D	Piping diameter [m];
E	Reaction activation energy [J/mol];
е	Viscous sub layer thickness or thermal boundary layer [m];
f	Friction factor [non-dimensional];
K	Global reaction constant [s ⁻¹];
$k_{_{lim}}$	Reference chemical reaction constants [s ⁻¹];
m _i	Deposited mass per unit surface $[kg/m^2]$;
Р	Probability of adhesion [nondimensional];
R	Universal ideal gas constant [8,314 J/(mol.K)];
Т	Medium absolute temperature [K];
T_{lim}	Absolute temperature atlimit operating conditions [K];
t , $t_a t_{lim}$ Time	e [s];
<i>u</i> _f	Fluid velocity [m/s];
X_i	Fouling thickness [m];

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Greek

Constants;
Fluid specific mass [kg/m ³];
Fouling specific mass $[kg/m^3]$;
Shear stress $[N/m^2]$;
Fluid dynamic viscosity [kg/(m.s)];
Friction velocity [<i>m</i> / <i>s</i>];
Kinematics viscosity $[m^2/s]$;
Wall roughness [m]

Subscripts

a	Adhesion;
f	Fluid;
i	Fouling;
W	Wall;