

A study of Transfer Rates of Phenols from Caustic to Crude Oil

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Abstract

Phenol and phenolic compounds are a common problem in various industries, due to their ability to dissolve in aqueous solutions, such as caustic. Caustic is used in several industrial operations for pH adjustments and for removing hydrogen sulfides from raffinated products. When the caustic is in contact with such products, phenols transfer to the caustic, and as a result the caustic leaves with a significant concentration of phenols causing problems in the waste-water treatment plant. Finding solutions for extracting phenols from spent caustic is therefore a major priority. The main purpose of this work was to investigate solutions for reducing the high phenols concentration in spent caustic at an oil refinery. Laboratory experiments and analysis were carried out in order to determine the mass-transfer rate of phenols and the potential for extracting phenols from caustic by contacting with crude oil. Plausible estimates for the over-all mass-transfer coefficient were made from the results obtained in an experimental setup. These estimates are useful for designing apparatus for treating streams with concentrated phenols. A solution for extracting the phenols in a specific caustic stream in a refinery, based on contacting the caustic with crude oil in a storage tank, was devised and the mass transfer coefficient in this particular system was estimated based on the experimental results. It is believed that this solution will be both cost efficient and practicable to implement.

1 Introduction

Water and caustic is used in various industrial operations. Processing operations may use water for cooling or washing processes, while caustic is

used for pH adjustments and, in the oil industry, removing hydrogen sulfides from products. This involves the water or caustic being in contact with a variety of media whereby mass transfer of components from these media to the water and caustic occurs. As a result, the waste water and caustic contain a number of chemical components, which can cause damage to the environment necessitating treatment in a dedicated a waste-water treatment plant.

The waste-water treatment plant, which is the focus of this project, is working at its maximum capacity at all times. As a consequence, this plant experiences challenges from time to time due to peak water loads. To increase the capacity of the the waste water treatment plant would require major investments, motivating this project to examine alternative methods for reducing the load on the plant.

About one-third of the total organic compounds in the waste water is phenolic compounds. Phenols are highly toxic; moreover, the water from refinery processes is often hot and volatile phenolic compounds may vaporize, which can lead to problems in the working environment at treatment plants.

The term phenol is applied in general to all derivatives of benzene that have a nuclear hydroxy group. Nuclear hydroxy is a functional group containing an oxygen atom bonded by covalent bonding to a hydrogen atom [1]. The compounds are termed mono-, di-, tri-hydric phenols etc., according to the number of hydroxy groups present. "Phenol" is the simplest form, where only one hydroxy group is bonded to the aromatic ring. Crude phenol was first isolated from coal tar, but later manufactured by cumene oxidation and by sulphonation. From petroleum cracking phenol, cresols and xylenols are formed [2]. Phenols are extremely toxic if inhaled or swallowed, have an injurious effect on humans, and are considered environmental pollutants [3]. In contact with skin and eyes phenols can cause acid burns. Even if diluted in water a phenol-containing solution can be irritating to skin and eye, and may also be toxic if inhaled or swallowed. A study [3] has shown that phenol itself is less toxic than substituted phenols.

1.1 Literature relevant to this work

Determining the physical parameters required to model the mass transfer of phenols between an organic and aqueous phase is not straight-forward but, due to the urgency of the problem, there is a considerable relevant literature. We briefly review some of the most recent papers.

Due to the interest in Canada in recovering valuable fossil-fuels from oil sands, also called tar sands, some literature on the diffusion of phenols

in bitumen has been published in the Canadian Journal of Chemical Engineering recently, mainly due to concerns about the environmental impact of volatilization of phenols.

Tang and Zhang [4], estimated experimentally and modelled the diffusion coefficient of phenol in bitumen under both steady and unsteady conditions. They used a desorption method proposed by Crank, where the cumulative flow leaving the bitumen into a well-stirred extraction phase was determined as function of time, and the diffusion coefficient determined on basis of this. Tang [5,6] in subsequent papers studied the volatilization and leaching into the environment of phenols from bitumen based on the model for phenol diffusion in bitumen developed in [4]. Ghavanati [7] reviewed the strengths and weaknesses of experimental methods for studying diffusion in bituminous materials, emphasizing the difficulty of determining concentration profiles in the opaque materials involved.

Cordova Villegas et al. [8] published a review of the processes available for removing phenols from waste water, discussing the merits and the limitations of each method. Their review includes processes such as distillation, absorption, extraction, chemical oxidation and electrochemical oxidation, but also more unconventional processes such as enzymatic processes, which they find are the most effective. Their review includes papers from the period 2013–2016 and includes 76 references, a testament to the rich literature dedicated to the subject.

Chen et al. [9] published a study where they identified the most promising organic solvents for extraction of phenols from aqueous phases. They initially screened a number of solvents using the COSMO-SAC model and on basis of this chose a few solvents for experimentation. They identified three ketones as being the most promising extractants.

Cui et al. [10] carried out work involving modelling, experimentation and simulations to improve an extraction process for polyphenols and phenols from wastewater by improving both the solvent used and the process design. They ended up using a compound solvent containing methyl isobutyl ketone and toluene in their improved extraction process. They found that the extraction process was complicated by much of the polyphenols being in the form of ionic dissociates.

Smirnova et al. [11] studied the extraction of phenols using various organic solvents, such as butyl acetate, methyl isobutyl ketone, from the water used in shale-chemical processes.

Ran et al. [12] studied the equilibrium data for phenols in the ternary system 2-pentanone-phenol -water at three different temperatures at ambient pressure. They compared their experimental results with empirical rela-

tions of Bachman and Hand and found good agreement. They concluded that 2-pentanone is an excellent solvent for the extraction of phenols.

While all these studies are relevant to the present work, none of them yield the data necessary for modelling the rate of phenol transfer between the specific phases available in our refinery (the same as are available in many refineries the world over), making the fundamental experimental study described here necessary and useful.

1.2 Objective of this work

The focus of this work is to devise practicable, cost-effective methods of reducing the concentration of phenols in the charge to a water treatment plant in a refinery to improve the working of this plant and avoid possible emissions of phenols to the environment due to occasional surges in the charge to the plant, exceeding its capacity. In the refinery there are opportunities to bring this aqueous stream in contact with crude oil, and doing this may be an attractive option to extract the phenols.

1.3 Some relevant transfer models

We recap that the two standard theories for mass transfer across interfaces [13] are the so-called “penetration theory” and the film theory due to Newton. The film theory may be best applicable for the mobile phase in a system where the other phase, or the interface between the phases itself, is immobile or near-immobile such that a diffusion film forms, responsible for most of the resistance to mass transfer in the mobile phase. The “penetration theory”, on the other hand, is based on the notion of constant renewal of the interface region by fluid pockets brought to, and removed from, the interface by turbulent eddies. The mass exchange with these pockets during the period of contact with the interface is calculated using the well-known penetration theory for the flow of heat or mass into or from an immobile phase or layer exposed to a constant temperature or concentration at the surface from time $t = 0$ [14]. This theory results in an average mass transfer coefficient for the period of contact with the surface, t_c of:

$$k_{av} = 2\sqrt{\frac{\mathbb{D}}{\pi t_c}} \quad (1)$$

To use this equation, the residence time distribution, $\psi(t)$ of the fluid pockets is required. The two standard models [15] for $\psi(t)$ are due to:

- a) Danckwerts, who proposed that the residence time of fluid pockets is random using a parallel with the residence time distribution of fluid elements in continuous stirred tank reactors, resulting in $\psi(t) = \frac{1}{\tau} \exp(-t/\tau)$ where τ is the mean residence time and
- b) Higbie, who proposed that all fluid pockets achieve the same residence time at the interface, θ , giving $\psi(t) = \frac{1}{\theta}$.

These two functions $\psi(t)$ give somewhat similar results for the mass transfer in practise [16].

The “penetration theory” (we use quotation marks to distinguish it from the well-known analytical theory for transfer of heat or mass in a solid wall or immobile fluid layer) may be best suited to systems where the two phases are fluid with a mobile interface between them. If one of the phases is immobile or near-immobile throughout, the mass transfer within that phase may best be modelled using the analytical penetration theory applied to the entire layer. Below a description of some more advanced, but time-tested, models based on the above-mentioned theories.

Toor and Marchello [16] proposed a hybrid between the film and “penetration” theories. They proposed that the mass transfer to or from fluid pockets with a short residence time by the interface may be found using the analytical penetration theory and that for fluid pockets with a long residence time by the interface by film theory. For fluid pockets with a residence time intermediate between the two, long enough for the concentration profile to penetrate the pocket but not long enough for a steady-state, linear concentration profile to be established, the transfer needs to be found from a more complex theory, which is worked out in the paper. Toor and Marchello experimentally investigated the transfer between a stirred liquid and a gas.

Harriott [17] offered an alternative to the theory proposed by Toor and Marchello and introduced a new model for mass transfer to an interface from a turbulent fluid. The eddies of the turbulent fluid are proposed to arrive at the interface region at random times and *at random distances from the surface*, i.e not all the pockets reach the interface but some undergo mass exchange while somewhat removed from the interface. Harriot’s model predicts that as the diffusivity decreases, the effect of the diffusivity on the mass transfer coefficient increases.

1.4 Experimental setup

The experimental setup used in this work consists of a transparent beaker containing an oil phase overlaying a caustic aqueous phase, the latter being

lightly stirred in most experiments using a magnetic stirrer. This is illustrated in the left part of Figure 1 where also the envisaged concentration profiles for phenol in the two layers are indicated.

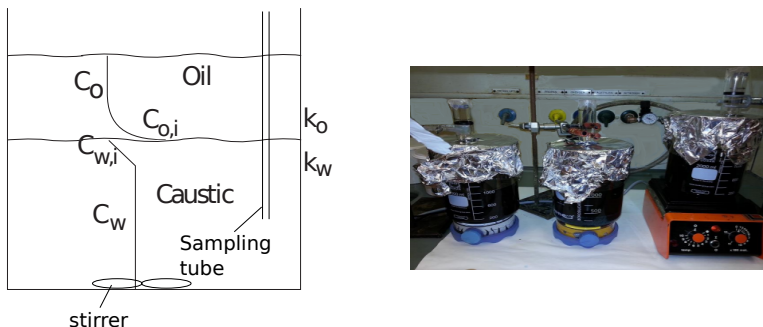


Figure 1: Left: Schematic of the experimental arrangements, indicating the concentration profiles of phenol in the two superposed layers of oil and caustic. k_o and k_w are the mass transfer coefficients for phenol in the oil and the caustic layer, respectively, and $C_{o,i}$ and $C_{w,i}$ the respective interface concentrations which are assumed in equilibrium, consistent with the “two-resistance” theory [13]. Right: photo showing an example of the three parallel experiments.

The equipment was assembled as shown in Figure 1. The beakers had a diameter of 12.75 cm. The spent caustic, the denser of the two phases, was added first. The sampling tube, to enable sampling of the bulk caustic layer without interfering with the superposed oil layer, was inserted to reach the middle of the caustic layer. The oil phase was then carefully added on top of the spent caustic layer, the oil comprising about 1/3 of the total fluid volume except in one experiment where the volumes of the two phases were reversed. It was crucial that no oil droplets entered the sampling tube when using this method. The beaker was sealed with aluminium foil to prevent evaporation as shown. Three parallels were done for each experiment to document repeatability.

This setup makes it possible to determine the mass transfer coefficient between the two phases directly, since the transfer area is known, while in most mass transfer literature only the product, kA , can be determined. The setup is also relevant to the envisaged process, since one solution for removing the phenols from the aqueous phase involves bringing this phase, in the form of a subposed layer, in contact with a crude oil phase in a storage

tank.

2 Experimental method

Systems consisting of a layer of crude oil of the type troll blend in contact with a layer of spent caustic, were arranged to study the effect on the phenol concentration in the caustic of contacting it with crude oil. The magnetic stirrer was used to create light turbulence in the spent caustic layer. The interface between the spent caustic and the crude oil, as well as the crude oil layer itself, was kept horizontal and immobile as much as possible in order to have a well-defined transfer area and to simulate the transfer of phenol from the caustic to the oil phase in an oil storage tank. The total duration of each experiment was 48 hours except for one longer experiment to study the attainment of equilibrium between the phases. A longer experiment of one week duration was also carried out to study the establishment of equilibrium as a function of time under the same experimental conditions.

2 ml samples were extracted from the middle of the spent caustic layer. These were collected at preset time intervals, and a spectrophotometer was used for analysing the concentration of phenols. The spent caustic has a strong unique colour of dark green, so that dilution with deionized water was necessary to use the spectrophotometric method. From previous work it was assumed the phenol concentration in the caustic was in the range of 8000–12 000 mg/l, therefore a calibrating curve for high phenols concentration was used.

The experimental conditions used are listed below. Only one parameter was changed at a time, keeping the rest of the parameters constant. The variations in experimental conditions, each of which was carried out to throw light on one of the options available in the refinery for achieving the desired extraction of phenols from the spent caustic, were as follows:

- Reducing the temperature to 10°C. This is the average temperature in the crude oil storage tank where the contacting with the caustic would take place.
- Increasing the pH of the caustic phase from 7.4 to 8.5 using 10M NaOH to study the effect of the pH and the state of dissociation of the phenols on the extraction process.
- Doubling the amount of crude oil, and halving the amount of spent caustic.

- Avoiding agitation of the caustic layer to simulated contacting in the crude oil storage tank
- Heavy shaking in a shaking machine to study the equilibrium concentrations of phenols in the two phases, and the conditions in a desalter, which was an alternative unit for oil-caustic contacting.
- Using different organic solvents on top of the spent caustic, kerosine and naphta, since near-by processing units for these solvents might also potentially be used for the extraction.

3 Results, analysis and discussion

To analyse the process we adopt the “two-resistance” model [13] assuming the resistance to mass transfer between the two phases is located in layers adjacent to the interface between them and there is no resistance over the interface itself. The transfer on the caustic side is therefore expressed by a mass transfer coefficient:

$$J = k_w(C_w - C_{w,i}) \quad (2)$$

where J is the molar flux of phenol, k_w is the mass transfer coefficient on the caustic side, and C_w and $C_{w,i}$ are the phenol concentration in the bulk and at the interface of the caustic layer, respectively. The driving forces on the two sides are the differences in chemical potentials between the bulk and the interface, and to express the mass transfer coefficient on the oil side, k_o , on the same basis as that on the water side we express the concentrations on the oil side in terms of their equivalents (i.e. those that would be in equilibrium with them [13]) in the caustic phase. Assuming a simple relationship between the equilibrium concentrations in the caustic and the oil: $C_{w,eq} = HC_{o,eq}$, where H is a distribution constant, we obtain:

$$J = k_o H(C_{o,i} - C_o) \quad (3)$$

Moving the two mass transfer coefficients to the LHSs and adding yields:

$$J \left(\frac{1}{k_w} + \frac{1}{k_o} \right) = (C_w - C_{w,i}) + H(C_{o,i} - C_o) = (C_w - HC_o) \quad (4)$$

the last equality because the two interface terms are equal since there is equilibrium at the interface.

The two resistances can be added to an over-all resistance: $\left(\frac{1}{k_w} + \frac{1}{k_o}\right) = \frac{1}{k}$. We do not know the concentration in the oil side, but we can generate an equation in C_w by realizing that $C_o V_o + C_w V_w = ph \Rightarrow C_o = \frac{ph - C_w V_w}{V_o}$, where ph is the total number of moles of phenol in the system and V_w and V_o are the volumes of the caustic and the oil phases, respectively. Also for the molar flow of phenol from the caustic to the oil: $JA = -\frac{dC_w}{dt} V_w$ where A is the area of the interface. Making these substitutions gives an equation in C_w :

$$-\frac{dC_w}{dt} \frac{V_w}{kA} = -\frac{Hph}{V_o} + C_w \left(1 + \frac{HV_w}{V_o}\right) \quad (5)$$

or:

$$a \frac{dC_w}{dt} = c + bC_w \quad (6)$$

with $a = -\frac{V_w}{kA}$, $b = \left(1 + \frac{HV_w}{V_o}\right)$ and $c = -\frac{Hph}{V_o}$. The solution of this equation is:

$$C_w(t) = -C_{w,i} \exp\left(\frac{b}{a}t\right) + \frac{c}{b} \left(\exp\left(\frac{b}{a}t\right) - 1\right) \quad (7)$$

with $C_{w,i}$ the initial concentration of phenol in the caustic phase. If this model, including the associated assumption of a flat, immobile interface between the phases, describes the system correctly it should be possible to fit this relation for $C_w(t)$ to the experimental values of $C_w(t)$ and glean the physical parameters from the fitted values of a , b and c . Taking the unknown physical parameters as ph , k and H , these can be found from:

$$k = -\frac{V_w}{aA}, \quad ph = -\frac{cV_w}{b-1} \quad \text{and} \quad H = \frac{(b-1)V_o}{V_w} \quad (8)$$

Figure 2 shows an example of a set of results for the phenol concentration in the caustic layer as a function of time together with the fitted expression (7). The fit parameters, which were determined by a multidimensional Rosenbrock search for the minimal sum of squared deviations between the experimental points and the model prediction, were: $a = -4.88 \times 10^5$, $b = 5.088$ and $c = -76.85$ giving: $k = 1.29E-07$ m/s, $ph = 0.0150$ mol and $H = 2.044$. The fit can be seen to be reasonably good (Pearson's $r=0.955$), confirming that the two-resistance model gives a good description of the system, the total phenol predicted, 0.015 mol, agrees well, as it did in all the experiments, with the measured initial amount of phenol in the caustic phase, 0.016 mol. Very little phenol is expected to be present in the crude oil phase initially, of the order of a few hundred μg per g [18]).

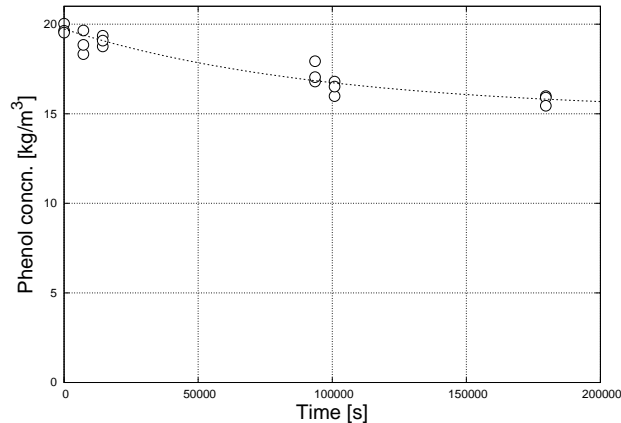


Figure 2: Experimental points for the concentration of phenol in the caustic layer, C_w , as a function of time using crude oil as solvent without stirring of the caustic layer, together with the fitted equation (7)

Figure 3 shows another example, this time for the experiment where a reduced temperature was used. The fit parameters were: $a = -8.35 \times 10^4$, $b = 3.21$ and $c = -56.59$ (Pearson's $r=0.985$) giving: $k = 7.54 \times 10^{-7}$ m/s, $ph = 0.0204$ mol and $H = 1.11$. The features compared to the previous set of results can be gleaned from the plot: it is clear that the equilibrium is reached earlier, but the final concentration in the caustic is higher, indicating that the phenol is less readily soluble in the solvent at this temperature. This is confirmed by the magnitude of the physical parameters, the mass transfer coefficient appears to be higher, which may be due to thermal convection in the system, while H is substantially lower at the lower temperature.

Table 1 summarizes the results of the experiments and of the fitting of the two-resistance model.

All but one of the experiments were, as mentioned, carried out over two days, the experiment marked "Eqm. Exp." was of a longer duration, namely one week, designed to study the attainment of equilibrium between the two phases under the approximate conditions that would prevail in the storage tank.

As mentioned, the experiment marked "more crude" was conducted with double the crude and half the caustic. It can be seen that total phenol is

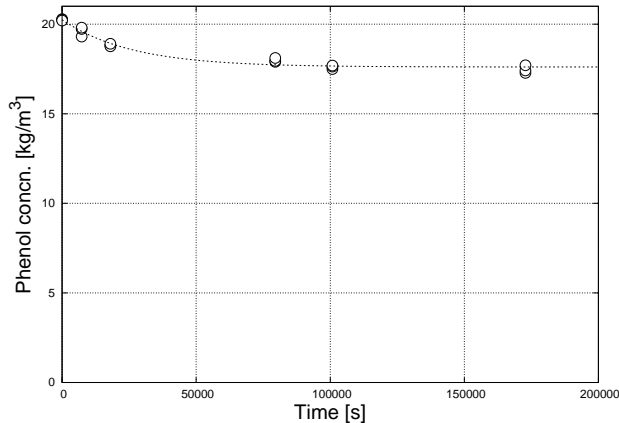


Figure 3: Experimental points for the concentration of phenol in the caustic layer, C_w , as a function of time using crude oil as solvent without stirring of the caustic layer and reducing the temperature of the system to 10°C during the experiment, together with the fitted equation (7)

half of that in the other experiments, confirming that most of the phenol initially is in the caustic phase, and very little is in the oil phase.

Most of the resistance to mass transfer is likely to be on the oil side. One way of estimating a lower-limit mass transfer coefficient on the oil side is to assume that this layer is quiescent, which will not be so in reality, and determine a mass transfer coefficient in the oil layer by applying penetration theory to this layer as a whole using Equation (1).

To use Equation (1) to estimate the mass transfer coefficient, we need the diffusivity, \mathbb{D} , of phenol in the crude oil, which we may roughly estimate from the empirical equation of Wilke and Chang, which is for binary, dilute mixtures of nonelectrolytes.

$$\mathbb{D}_{AB} = \frac{(7.5 \times 10^{-8})(\psi M_B)^{\frac{1}{2}} T}{\mu V_A^{0.6}} \quad (9)$$

Although the crude oil/phenol mixture is not a binary system, we use this as a rough estimate. Here M_B is the molecular mass of the solvent, taken as 0.318 kg/mol for the crude [19], T is the temperature, μ is the viscosity of the solution, taken as 4.849 cP [20], V_A is the molar volume of the

Table 1: Summary of the experimental results and the physical parameters gleaned from them

Experiment	a	b	c	k [m/s]	ph [mol]	H [-]
No stirring	-4.88×10^5	5.09	-76.9	1.29×10^{-7}	0.0150	2.04
With stirring	-3.14×10^4	4.34	-69.6	2.00×10^{-6}	0.0166	1.67
Reduced temp.	-8.35×10^4	3.21	-56.6	7.54×10^{-7}	0.0204	1.11
Increased pH	-3.44×10^4	4.71	-68.5	1.83×10^{-7}	0.0149	1.85
Kerosene	-2.53×10^5	4.38	-65.7	2.49×10^{-7}	0.0155	1.69
Naphta	-6.28×10^4	4.35	-69.0	1.00×10^{-6}	0.0164	1.68
More crude	-4.72×10^4	1.95	-19.8	6.68×10^{-7}	0.00835	1.90
Eqm. Exp.	-2.53×10^5	4.38	-65.7	2.49×10^{-7}	0.0155	1.69

diffusing solute, taken from the material safety dat sheet for phenol to be $87.8 \text{ cm}^3/\text{mol}$ and ψ is the association parameter for the solvent, for which a value of unity is recommended for non-polar liquids [21].

The phenol diffusivity in crude oil at room temperature from Equation (9) comes out to be $5.48 \times 10^{-10} \text{ m}^2/\text{s}$ giving a mass transfer coefficient from Equation (1) of $k_o = 5.91 \times 10^{-8} \text{ m/s}$, which is lower that would have been expected from the overall mass transfer coefficients listed in Table 1, but is reasonable in view of the fact that disturbance of the liquid oil layer will have taken place during all the experiments.

All the experiments are seen to give reasonable and consistent results, in light of the scatter in the results. Figure 2 is, as far as the scatter is concerned, more typical than Figure 3. The three parallel experiments made it quite straightforward to quantify the error in the measurements. A pooled standard deviation, s_p , was computed as:

$$s_p = \sqrt{\frac{\sum_{i,j} (y_{i,j} - \bar{y}_j)^2}{d.f.}} \quad (10)$$

where j denotes the measurement of the concentration at any given time, and $i = 1, 3$ denotes one of the parallel experiments. $d.f.$, the degrees of freedom is the number of measurements minus the number of means, \bar{y}_j , determined. The pooled standard deviation came out to be 0.675, and the standard deviation of the means of the three parallel experiments should therefore be $0.675/\sqrt{3} = 0.39 \text{ mol/m}^3$.

4 Conclusions and prospects

- An experimental method useful for studying the extraction of phenols from waste caustic or any aqueous stream, has been designed and tested.
- The two-resistance model was found to be successful in describing the system and the magnitudes of all the physical parameters gleaned from fitting this model to the experiments were plausible.
- The results were mutually consistent and they showed that crude oil is an acceptable solvent for the extraction of phenols from aqueous phases in the sense that the absorption of phenol by the crude oil was sufficient for offloading the water treatment plant and the rate of transfer was sufficient to provide the pretreatment capacity required upstream of the water treatment plant.
- reducing the temperature at which the extraction takes place from room temperature to 10°C has a substantial effect in reducing the over-all mass transfer coefficient and the distribution coefficient which decreased from approximately 2 at room temperature to 1 at 10°C.
- Equilibrium was reached in approximately two days agitating the system only slightly.

While this study focused on answering particular questions related to the operation of the refinery, the experimental method is suitable for a wider study of phenols extraction. Aspects that emerge as interesting from this study are the effects of temperature and phenols concentration on the transfer and the transfer of different specific phenols.

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