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TÍTULO DO TRABALHO:

Numerical evaluation of temperature and concentration profiles obtained from petroleum waste pyrolysis

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Resumo

A indústria petrolífera gera vários resíduos ao longo da cadeia de produção. Para mitigar os impactos ambientais, diversos processos são desenvolvidos para converter esses resíduos em materiais menos nocivos ou com valor energético agregado. Para estudar e compreender as alternativas de tratamento destes resíduos, o presente trabalho propõe uma análise cinética, utilizando a equação de Arrhenius, das espécies envolvidas no processo de pirólise, um processo de conversão termoquímica numa atmosfera inerte. Portanto, é desenvolvido um modelo numérico no mathematica unidimensional e isotérmico para um leito de fluxo descendente. O artigo descreve um modelo cinético de uma única fase de desvolatilização para a pirólise de resíduos de petróleo, onde são produzidos gases não condensáveis, char e espécies mais pesadas como Fenol (C_6H_6O), Naftaleno ($C_{10}H_8$) e Benzeno (C_6H_6), que são posteriormente craqueados termicamente. A composição do produto de desvolatilização é prevista por balanços de massa elementares para o resíduo CxHyOz, dados por valores experimentais correlacionados com a análise elementar do material. Este modelo permite a análise da formação do produto para determinadas temperaturas fixas e composição elementar do resíduo. A apresentação dos resultados fornece informações sobre o comportamento das espécies, incluindo o seu consumo e produção, que são analisados através das leis fundamentais de conservação de massa, permitindo compreender o comportamento do produto formado.

Palavras-chave: Pirólise, Resíduos de petróleo, Análise cinética, Conversão termoquímica, Leito Downdraft.

Abstract

The petroleum industry generates various residues, such as oil sludge, throughout the production chain. In order to mitigate the environmental impacts, diverse technologies are developed to convert these residues into less harmful materials or materials with added energy value. To study and understand treatment alternatives for these wastes, the present work proposes a kinetic analysis using the Arrhenius equation of the species involved in Oil Sludge pyrolysis, a thermochemical conversion process in an inert atmosphere. Therefore, an one-dimensional and isothermal numerical model is developed in Mathematica for a downdraft bed (DB) reactor. This paper describes a kinetic model of a single devolatilization phase for the pyrolysis of petroleum residues, where non-condensable gases, char, and heavy hydrocarbons such as Phenol (C_6H_6O), Naphthalene ($C_{10}H_8$) and Benzene (C_6H_6) are produced, which are subsequently thermally cracked. The composition of the devolatilization product is predicted by elemental mass balances of the feedstock CxHyOw, given by experimental values correlated to the elemental analysis of the material. This model allows product formation analysis at certain fixed temperatures and the elemental composition of the residue supplied. The presentation of results provides information on species' behavior, including their consumption and generation, which are analyzed through the fundamental laws of mass conservation, allowing for an understanding of the formed product's behavior.

Keywords: Pyrolysis, Petroleum residues, Kinetic analysis, Thermochemical conversion, Downdraft bed.

Introduction

The widespread exploration and production of oil significantly impact the environment. According to Hu, Li, and Zeng (2013), these activities contribute to atmospheric pollution, water contamination, and damage to land flora, generating harmful wastes that require treatment to prevent ecosystem disruption. Despite these concerns, oil and gas are vital to the global economy and energy supply, requiring effective waste treatment methods to mitigate environmental harm and safeguard social well-being.

This study focuses on oil sludge (OS), a toxic residual substance from refining operations and petrochemical processes. OS contains harmful substances like bacteria, polycyclic aromatic hydrocarbons (PAHs), and heavy metals. Its transportation and storage can cause secondary pollution, affecting human health (Wang et al., 2020). González et al. (2019) note that every 500 tons of processed oil produces about 1.0 ton of OS, with Brazilian refineries generating around 0.22 million tons annually. Sustainable methodologies for managing OS include chemical, thermal, and thermochemical processes. Bahng et al. (2009) list methods such as landfill deposition, incineration, solidification/stabilization, centrifugation, and solvent extraction, though many have limited sustainability due to low-value by-products. Preferred thermal processes like combustion, pyrolysis, and gasification efficiently manage organic solids and produce valuable by-products, such as gaseous and liquid fuels with high hydrocarbon content (Castillo et al., 2021; He et al., 2019). Pyrolysis, a promising technology, decomposes organic waste at moderate temperatures (300-600°C) without oxygen, producing bio-oil, non-condensable gases (NCG), and biochar. NCG, composed of hydrogen, carbon monoxide, and methane, can be used as an energy source or fuel precursor (Hui et al., 2020), offering a sustainable waste management solution by reducing waste volume and providing valuable products (Sharma et al., 2019).

Song *et al.* (2019) put forth a methodology for collecting pyrolysis oil, which entails mixing oily sludge with steel slag. The experiment demonstrated that at 550 °C, the tar yield can reach 10.63%. In the pyrolysis process at 650 °C, the production of hydrogen (H_2) and methane (CH_4) was enhanced to a greater extent, reaching maximum values of 26.43% and 34.45%, respectively. Huett et al. (2019) worked on an experimental study of wood pyrolysis, where the composition of the NCG was analyzed at different temperatures, where the highest production of H_2 was observed at 900°C, reaching 22.3% molar, while CO production increased to 47.6% molar at the same temperature. The H_2/CO ratio increased from 0.3 at 600°C to 0.5 at 900°C.

This article aims to develop and present a numerical mass conservation model of the oil sludge pyrolysis process, focusing on chemical kinetics. In this manner, an analysis of the behaviors of the species along the bed is provided, supplemented by a qualitative evaluation of the system's parameters. In order to achieve this, a simplified conservation model has been developed using Wolfram Mathematica software.

Theoretical formulation

In order to develop this work, the problem in question is approached conceptually by unraveling the conservation laws involved. The model considers a downdraft pyrolysis reactor, which introduces the OS at the upper end. The char and syngas are extracted from the lower streams, as illustrated in Figure 1.

For the model implementation, it was necessary to define simplifications that would counteract the phenomenological complexity of the problem in question.

- There is only one homogeneous phase in the reactor. Based on the similarity of a thin layer model, where the solid fuel has a thin layer compared to the gaseous phase, facilitating heat transfer and making heating uniform (Song et al., 2024).
- The drying stage is instantaneous. Thus, the heat transfer rates help to ensure that the temperature inside the particles is homogeneous (Castillo Santiago et al., 2021)

- Char can be considered pure carbon (Smith Lewin et al., 2020).
- Mass transfer occurs only by convection.

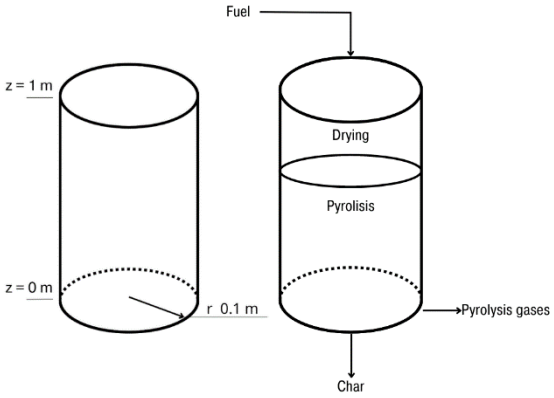

Figure 1: Control volume schematic

Mass conservation

The conservation of mass in the system is governed by equations (1) and (2) derived from the initial problem formulation.

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho v) \tag{1}$$

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (C_i v - \vartheta_i \nabla \omega_i) = \overline{r}_i \tag{2}$$

In this context, ρ and v represent the specific mass and velocity of the mixture, respectively, while ω_i, C_i, and $\overline{r}_i$ denote the mass fraction, volumetric concentration, and consumption (or generation) rate of species i, respectively. The Fick's Law mass diffusivity of a given species i is represented by ϑ_i, and according to Barrozo and Benedetti (2016), it depends on the temperature, as shown in Eq. (3)

$$\vartheta_i = \theta_{i,0} \exp\left(\frac{-E_i}{RT}\right) \tag{3}$$

Where E_i represents the activation energy of a species i and R is the gas constant.

Chemical kinetics

In the proposed model, ten species were considered [H_2, CO, CO_2, CH_4, H_2O, C, $C_{10}H_8$, C_7H_8, C_6H_6, and OS ($C_{59}H_{88}O$)]. Table 1 enumerates the studied reactions, where the following are noted as j_1 to j_8. In the drying zone, liquid water transforms into steam without any chemical reaction. In the pyrolysis zone, the OS devolatilization occurs, followed by thermal cracking of naphthalene and dry and steam reforming of toluene and benzene.

Table 1: Considered reactions

j	Reaction name	Stoichiometry
1	OS Devolatilization	$4C_{57}H_{85}O \rightarrow C + 18C_{10}H_8 + 45CH_4 + CO + CO_2 + 7H_2 + H_2O$
2	Naphthalene Cracking	$2C_{10}H_8 \rightarrow 12C + C_7H_8 + CH_4 + 2H_2$
3	Toluene Reforming	$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$
4	Catalytic toluene reforming	$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2$
5	Toluene Dry Reforming	$C_7H_8 + 7CO_2 \rightarrow 14CO + 4H_2$
6	Toluene Hydrodealkylation	$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$
7	Benzene Reforming	$C_6H_6 + 12H_2O \rightarrow 6CO_2 + 15H_2$
8	Drying	$H_2O_{(l)} \rightarrow H_2O_{(v)}$

The chemical formula of the sludge $C_vH_wO_xN_yS_z$ is approximately $C_yH_wO_x$. Considering that the sulfur (S) and nitrogen (N) species are elements treated as inert in the pyrolysis stage, they are analogously not considered for the mass balance of the species. This work uses the composition of the sludge characterized by Castillo Santiago et al. (2023)

The production and consumption rates of the species are determined by the reactions illustrated in Table 1. In general, the equation is given as follows:

$$\overline{r}_i = M_i \sum_{j=i}^{8} \mu_{i,j}\ \dot{r}_j\ , \quad i = 1,2,\dots 10. \tag{4}$$

The term $\mu_{i,j}$ represents the stoichiometric coefficient of species i in reaction j, where it is positive if the species is generated and negative if consumed. $\dot{r}_j$ represents the velocity of the reaction and is described by the kinetics of each reaction, which depends on the temperature and molar concentration of the species involved. The rate law used is a generalized power law for all the reactions present, given by Eq. (5).

$$\dot{r}_j = A_j\ Exp\left(\frac{-E_{a,j}}{RT}\right)\left[C_yH_w\right]^{\alpha}[H_2]^{\beta}[H_2O]^{\lambda}[CO_2]^{\xi}T \tag{5}$$

Where A_j and $E_{a,\,j}$ are the pre-exponential factor and activation energy of the Arrhenius equation, respectively. For the global velocity law consideration, the reaction kinetics depend on the molar concentrations of the hydrocarbon volatiles (C_yH_w), H_2, H_2O, and CO_2, as well as the average temperature of the bed (T). The kinetic parameters (A_j and $E_{a,j}$) and the reaction orders obtained from the literature for each reaction j considered are shown in Table 3.

Table 2: Kinetic parameters

j	$A_j\ (mim^{-1})$	$E_{a,j}$ ***Kj/Kmol***	α	β	λ	ξ	***References***
1	1.52×10^3	1.05×10^5	1	0	0	0	Zhang et al., 2014
2	1.7×10^{14}	3.5×10^5	1.6	0	0	0	Qian; Kumar, 2017
3	3.3×10^{10}	2.47×10^5	1	0	0	0	Qian; Kumar, 2017
4	3.3×10^{10}	2.47×10^5	1	0	0	0	Qian; Kumar, 2017b
5	3.3×10^{10}	2.47×10^5	1	0	0	0	Qian; Kumar, 2017b
6	3.3×10^{10}	2.47×10^5	1	0	0	0	Qian; Kumar, 2017b

7	2.0×10^{16}	4.43×10^{5}	1.3	0.4	0	0	Ji et al. 2009
8	5.13×10^{10}	8.8×10^{4}	0	0	1	0	Gómez-Barea et al. 2010

NUMERICAL SOLUTION

Based on the simplifications and given the control volume in Figure 1, considering that the temperature and pressure gradients in the direction transverse to the flow are negligible, the system operates in a permanent regime, and the effects of diffusion are neglected, so Eq. (1) and (2), are reduced as:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial z}(v_z \rho) = 0 \;\rightarrow\; \frac{\partial}{\partial z}(v_z \rho) = 0 \tag{6}$$

$$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial z}(v_z C_i) = \frac{\partial}{\partial z}\left(\rho D_i \frac{\partial \omega_i}{\partial z}\right) + \overline{r}_i \;\rightarrow\; \frac{\partial}{\partial z}(v_z C_i) = \overline{r}_i \tag{7}$$

$$\frac{\partial v_z}{\partial t} + v_z \frac{\partial v_z}{\partial z} = 0 \;\rightarrow\; v_z \frac{\partial v_z}{\partial z} = 0 \tag{8}$$

The momentum equation Eq. (8) leads to a constant mixing velocity, such that:

$$v_z \frac{\partial \rho}{\partial z} = 0 \tag{9}$$

$$v_z \frac{\partial C_i}{\partial z} = \overline{r}_i \;,\; i = 1,2,\ldots,10 \tag{10}$$

Accordingly, as the specific mass of the OS (ρ) remains constant, only Eq. (10) seeks numerical solutions in the model developed. Thus, as the system of non-linear ordinary differential equations is generated, the NDSolve function in Mathematica is employed to obtain the numerical solutions. The boundary conditions are specified at the entrance to the pyrolysis reactor, where the OS feed occurs. These are given as follows:

$$z = 1\,m \;,\; C_i(1) = 0 \;,\; i = 1,..,9 \tag{11}$$

$$v_z A_z C_{10}(1) = \dot{m}_{\,in,\,os},\; C_{10}(1) = \rho \tag{12}$$

$$v_z A_z C_5(1) = \dot{m}_{\,in,\,water},\; C_5(1) = \phi\rho \tag{13}$$

$\dot{m}_{\,in,\,os}$, is the OS flow rate at the pyrolysis reactor inlet, a known value, and the OS concentration is given by its specific mass. $\dot{m}_{\,in,\,water}$ represents the mass flow rate of water at the reactor inlet, which is given by the humidity of the OS (ϕ) and the specific mass.

Results and Discussion

Two scenarios were examined under isothermal conditions for a flow rate of 3.6 kg/h of OS, with the primary outcomes of implementing the proposed numerical model presented. The first scenario was conducted at a pyrolysis temperature of 650 °C (Figure 2) and the second scenario at 700 °C (Figure 3). Qualitative interpretations of the species' behavior in each case were developed from this.

Figure 2a shows the formation of significant volatiles and char as the OS is consumed along the bed, while Figure 2b shows the heaviest hydrocarbons. At 650 °C, at the 0.4 m point of the reactor, all species reach a permanent regime, indicating a balance in the rate of generation and consumption. Initially, the main species produced are CH_4 and char due to degassing (j1). From 0.95 m, the reforming

and cracking reactions (j2-j5) intensify, consuming naphthalene and producing toluene, CO, char, and H_2. At the 0.8 m position, toluene Hydrodealkylation (j6) produces benzene, consuming toluene, as shown in Figure 2b.

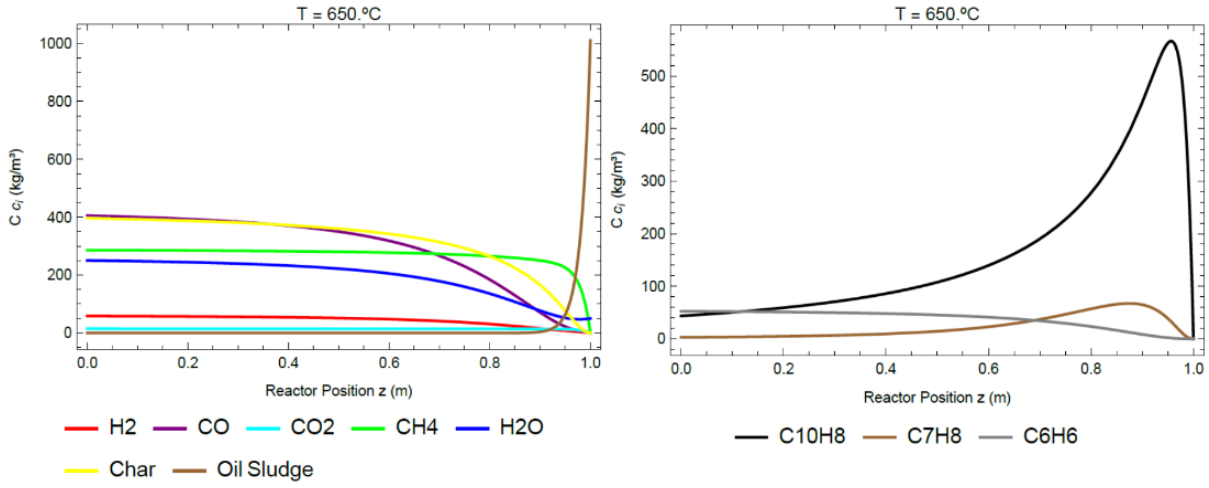

Figure 2: concentrations of the species along the bed at a temperature of 650 °C. Main species (2a) and Tar products generated (2b)

The results shown in Figure 3 are analogous to the analysis previously performed in Figure 2. This case occurs at a pyrolysis temperature of 700°C and presents a regime of permanence at 0.95 m in Figure 3a and 0.8 m in Figure 3b. This difference with the previous case at 650°C is due to the higher reaction rate of the species in the bed, whose kinetics depend on the temperature as indicated by Arrhenius term of Eq. (5) and according to reported by Mostafa *et al.* (2015). It is worth noting that reactions with higher activation energies vary more with temperature, which is observed in the linearization of the Arrhenius equation.

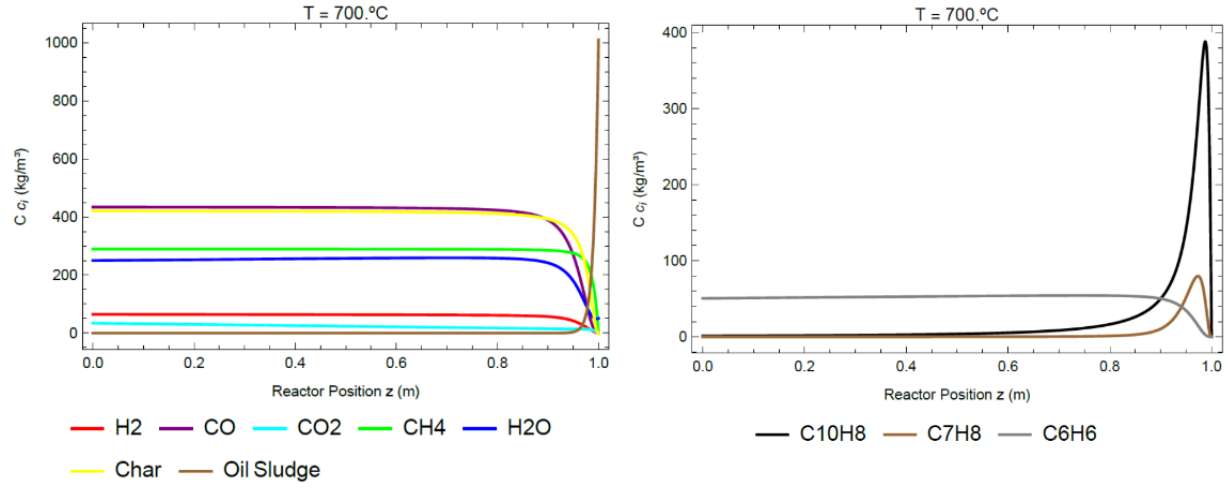

Figure 3: concentrations of the species along the bed at a temperature of 700 °C. Main species (3a) and Tar products generated (3b)

Conclusion

In conclusion, this study presents constructive results for the qualitative analysis of the mass conservation model with a kinetic approach to oil sludge pyrolysis, with simplified problem modeling. These behaviors observed in the species present facilitate comprehension of the system and evaluation of new conditions and strategies for developing more complex models. The results highlight the pivotal role of temperature in influencing reaction rates and the distribution of final products, thereby establishing a foundation for future optimizations in thermochemical processes. At 700°C, higher reaction rates are observed, particularly for reactions with higher activation energies, which result in different residence times in the reactor bed compared to 650°C. At 650°C, the initial products are methane and char, while subsequent reactions yield toluene, carbon monoxide, char, and hydrogen. This work contributes to advancing the understanding of pyrolysis and the operating conditions that can be adjusted in more complete models to maximize efficiency and the desired product yield.

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References

CASTILLO SANTIAGO, Y. et al. Assessment of the energy recovery potential of oil sludge through gasification aiming electricity generation. **Energy**, v. 215, 15 jan. 2021.

EL-SAYED, S. A.; MOSTAFA, M. E. Kinetic Parameters Determination of Biomass Pyrolysis Fuels Using TGA and DTA Techniques. **Waste and Biomass Valorization**, v. 6, n. 3, p. 401–415, 18 jun. 2015.

GÓMEZ-BAREA, A.; LECKNER, B. Modeling of biomass gasification in fluidized bed. **Progress in Energy and Combustion Science**, v. 36, n. 4, p. 444–509, 1 ago. 2010.

JI, P.; FENG, W.; CHEN, B. Production of ultrapure hydrogen from biomass gasification with air. **Chemical Engineering Science**, v. 64, n. 3, p. 582–592, 1 fev. 2009.

Castillo Santiago, Y., Pérez, J. F., & Sphaier, L. A. (2023). Reaction-front and char characterization from a palm kernel shell – Oil sludge mixture under oxygen lean regimes in a fixed-bed gasifier. *Fuel*, *333*. https://doi.org/10.1016/j.fuel.2022.126402

PRASERTCHAROENSUK, P.; BULL, S. J.; PHAN, A. N. Gasification of waste biomass for hydrogen production: Effects of pyrolysis parameters. **Renewable Energy**, v. 143, p. 112–120, 1 dez. 2019.

QIAN, K.; KUMAR, A. Catalytic reforming of toluene and naphthalene (model tar) by char supported nickel catalyst. **Fuel**, v. 187, p. 128–136, 1 jan. 2017a.

QIAN, K.; KUMAR, A. Catalytic reforming of toluene and naphthalene (model tar) by char supported nickel catalyst. **Fuel**, v. 187, p. 128–136, 1 jan. 2017b.

SMITH LEWIN, C.; FONSECA DE AGUIAR MARTINS, A. R.; PRADELLE, F. Modelling, simulation and optimization of a solid residues downdraft gasifier: Application to the co-gasification of municipal solid waste and sugarcane bagasse. **Energy**, v. 210, 1 nov. 2020.

SONG, Q. et al. Characterization of the products obtained by pyrolysis of oil sludge with steel slag in a continuous pyrolysis-magnetic separation reactor. **Fuel**, v. 255, 1 nov. 2019.

ZHANG, Y. L. et al. Heterogeneous cracking reaction of tar over biomass char, using naphthalene as model biomass tar. **Energy and Fuels**, v. 28, n. 5, p. 3129–3137, 15 maio 2014.

Sidineia Barrozo and Assis Vicente Benedetti. COMPREENSÃO MATEMÁTICA DA DIFUSÃO NO CONTEXTO ELETROQUÍMICO. Quimica Nova, 39(3):356–370, 2016. doi: <10.5935/0100-4042.20150179>. Citado na página 26.