

Investigation of Reaction Pathways and Kinetics of Turkish Asphaltenes

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In this study, reaction kinetics of asphaltene fractions of petroleum feedstocks from field in southeastern part of Turkey were investigated. Asphaltene was fractionated from atmospheric residue of petroleum feedstock. Atmospheric petroleum residue was obtained by removing the distillates boiling up to 350 °C using atmospheric distillation. Asphaltenes were subjected to pyrolysis reactions at 350, 375 and 400 °C for holding times ranging from 10 and 120 min. Product fractions were separated as gas, maltene, remaining asphaltene and coke. The time and temperature dependence of product distributions were determined.

Four-lump model was proposed to explain the reaction pathways. This kinetic model was described as a system of ordinary differential equations. In order to estimate the rate constants in these ODEs, a Matlab code has been developed. Order of reaction is another important subject for fitting, first-order for all reactions and second-order for all reactions were analyzed.

1. Introduction

Asphaltenes are the aromatic-soluble and paraffinic-insoluble fraction of crude oils. Heavy crude oils contain higher asphaltene contents compared to lighter crude oils. Asphaltenes contain condensed aromatic rings branched with aliphatic chains (Calemma et al., 1998). They are complex black solid fractions of petroleum and researchers suggest that asphaltenes are mostly responsible for coke formation. Asphaltenes cause many problems during refining procedures. Coke is the primary cause of catalysts deactivation during refinery process. Coke and metal atoms are precipitated on the catalyst surface and block the pore mouth so the useful life of the catalyst decreases (Speight, 1991).

The heavier fractions of petroleum are not so useful. These fractions need to be converted into lighter and more useful products. A petroleum refinery, converting heavier hydrocarbons to lighter hydrocarbons depends on technologies. The majority of the heavy fractions are non-volatile, high molecular weight and metal-containing asphaltenes. Heat treatment processes are problematic on asphaltenes depending on coke formation and catalyst poisoning. For this reason understanding the thermal-cracking behavior of asphaltenes is base case for oil industry.

Over the past three decades various scientific research studies have been conducted on relations between asphaltene structures and their physical and chemical properties (Chrisman et al. 2009). Several procedures have been applied in the literature for investigation of molecular structure of asphaltene such as molecular weight determination (Miller et al., 1998), functional group determination by FTIR spectrometer (Hasan et al., 1988) In recent years, studies on pyrolysis kinetics of asphaltenes have become important due to economic and efficiency reasons (Zhao et al. 2011;).

Yasar et al. (2001) carried out experimental studies to investigate the effect of reaction conditions on the reaction pathways and selectivities with the resid and asphaltenes. Reaction medium compounds were separated into four main classes of asphaltene, maltene, gas and coke then experimental data was attempted to fit Four-lump model. Coke did not occur in this model directly from Malten. The followed path is Malten -> Asphaltene -> Coke. Banerjee et al. (1986) also concluded that coke formation increased with

the degree of aromaticity of the fractions of crude oils. Al Humaidan et al. (2013) studied a thermal cracking kinetic model with five-lump model.

In this study, in order to understand the behaviour of the thermal decomposition reactions of asphaltenes, the suitability of Four Lump model was examined. In addition, using the experimental data kinetics and selectivity of reactions are also discussed.

2. Experimental

2.1 Material

Crude oil samples, used in the studies, were obtained from Turkish Petroleum Corporation and samples belong to Besikli and Garzan regions. They were directly used without any prior chemical processing. N-heptane and toluene from Merck were used to obtain asphaltene. 28 x 80 mm Macherey - Nagel cellulose cartridges were used for soxhlet extraction.

2.2 Asphaltene Separation

Atmospheric petroleum residue was obtained by removing the distillates boiling up to 350 °C using atmospheric distillation. Asphaltene fraction was prepared from the atmospheric residue. Residue was added to n-heptane in a 1 to 40 weight ratio. The solution was stirred for 1 h at 60 °C, and then allowed to cool under continuous stirring for 4 h. The solution was then allowed to settle overnight prior to filtering. The solution was filtered to remove the asphaltene precipitate. The asphaltene was subjected to Soxhlet extraction to verify the absence of maltenes. Likewise, boiling heptane was used to extract the asphaltenes to remove any residual maltenes. Solvent was removed by rotary evaporation. Also, extracting the asphaltenes with boiling toluene revealed the absence of coke in the residue (Yasar et al. 2007, Yasar et al. 2001).

2.3 Asphaltene Pyrolysis

Mettler Toledo 822e Differential Scanning Calorimeter (DSC) was used for the pyrolysis reactions. Briefly, glass tubes which were special for DSC containing samples were loaded into the furnace of DSC. They were purged several times with high pressure argon to provide an inert environment for reactions. Glass tubes containing asphaltene were closed by melting and subjected to pyrolysis reactions at 350, 375 and 400 °C for holding times ranging from 10 and 120 minutes using DSC. After the desired reaction time had elapsed, product fractions were separated as gas, maltene, remaining asphaltene and coke by using gooch crucible. Glass tubes were broken and the gas yields were determined gravimetrically. Maltens were eluted with heptan. Maltens were collected until the heptane remained colorless. The maltene yields were determined by evaporating the heptane and weighing malten remaining. Subsequently, remaining asphaltenes were separated with toluen from the gooch crucible. Asphaltene yields were determined by weighing the solid remaining after solvent removal. Then, insoluble solids, cokes in the gooch crucible were dried and weighed to determine the yields of coke (Yasar et al. 2001, Yasar et al. 2007).

3. Kinetic Model

3.1 Four Lump Model

Pathways for the Four-Lump model are given in Figure 1.

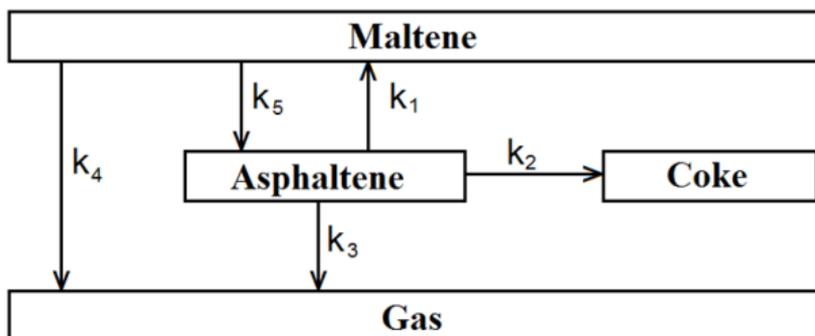


Figure 1: Lumped resid/asphaltene model.

and differential equations,

$$\frac{dy_A}{dt} = k_5 \cdot y_M^n - k_1 \cdot y_A^m - k_2 \cdot y_A^m - k_3 \cdot y_A^m \quad (1)$$

$$\frac{dy_M}{dt} = k_1 \cdot y_A^m - k_5 \cdot y_M^n - k_4 \cdot y_M^n \quad (2)$$

$$\frac{dy_G}{dt} = k_3 \cdot y_A^m + k_4 \cdot y_M^n \quad (3)$$

$$\frac{dy_C}{dt} = k_2 \cdot y_A^m \quad (4)$$

where y_A , y_M , y_G and y_C are the weight fraction of asphaltene, maltene, gas and coke respectively, k values are apparent rate constants, n and m are the apparent reaction orders for the model (Zhao et al. 2011).

3.2 Optimization and Parameter Estimation

Given the experimental weight fractions of the four lumps, interior point approach was used to estimate the five rate constants, which are the model parameters given in Eqs. (1-4). The solution algorithm minimizes the objective function which defined as sum of square error (SSE) between the experimental and predicted weight fractions.

Coefficient of determination (R^2) is defined as according to AlHumaidan et al. (2013):

$$R^2 = \frac{SST - SSE}{SST} \quad (5)$$

$$SSE = \sum_{i=1}^N (y_i^{\text{exp.}} - y_i^{\text{pred.}})^2 \quad (6)$$

$$SST = \sum_{i=1}^N (y_i^{\text{exp.}} - \bar{y})^2 \quad (7)$$

N is the number of lumps, $y_i^{\text{exp.}}$ and $y_i^{\text{pred.}}$ are the experimental and predicted weight fractions of lump i , respectively, while \bar{y} is the average of the experimental weight fractions.

4. Results and Discussion

The relative percentages of the reaction products of Besikli and Garzan asphaltene which are gas, malten, remaining asphaltene and coke are shown in Figure 2 and Figure 3. The amounts of gas were smaller at 350 °C than the amounts of gas at 375 and 400 °C. The amount of remaining asphaltene is highest at 350 °C for 10 minutes and is minimum at 400 °C for 120 minutes.

The temporal variations of the maltene yield are illustrated in Figure 2 and Figure 3. Maltenes were more abundant than gases at all times and temperatures. Although the maltene yield increased at reaction temperatures, the amount of maltenes decreased after 20 minutes at 350 °C and 400 °C and after 40 minutes at 375 °C for Garzan asphaltene pyrolysis reactions. Yasar et al. (2001) also found the same result about disappearance of maltene with respect to time. The disappearance of maltene indicated the secondary cracking and possible condensations. The amount of malten increased at reaction temperatures for Besikli asphaltene pyrolysis reactions.

Figure 2 and Figure 3 show the temporal variations of remaining asphaltene for the three reaction temperatures and the temporal variations of coke yield for the three reaction temperatures. As temperature rose, the disappearance rate of asphaltenes increased and as temperature rose, the appearance rate of coke increased.

The pyrolysis at 375 and 400 °C yielded more coke and gas and less remaining asphaltene if compared with pyrolysis at 350 °C.

The experimental results are used to propose Four-lump model to explain the reaction pathways. This kinetic model is described as a system of ordinary differential equations. In order to estimate of the rate constants in these ODEs, it has been developed a Matlab code. The model describes the system for $n=2$, $m=2$ indicating a strong correlation between experimental and predicted values as shown in Table 2 R^2 column. So the four lump model can be used to predict asphaltene pyrolysis rate coefficients. This manner is also shown in ($n=2$, $m=2$) cases fits the experimental data better than ($n=1$, $m=1$).

In almost every case four lump model fits better at higher temperatures. This situation is valid for both of reaction orders used in this study. This circumstance can be seen in Table 2, Figure 2 and Figure 3.

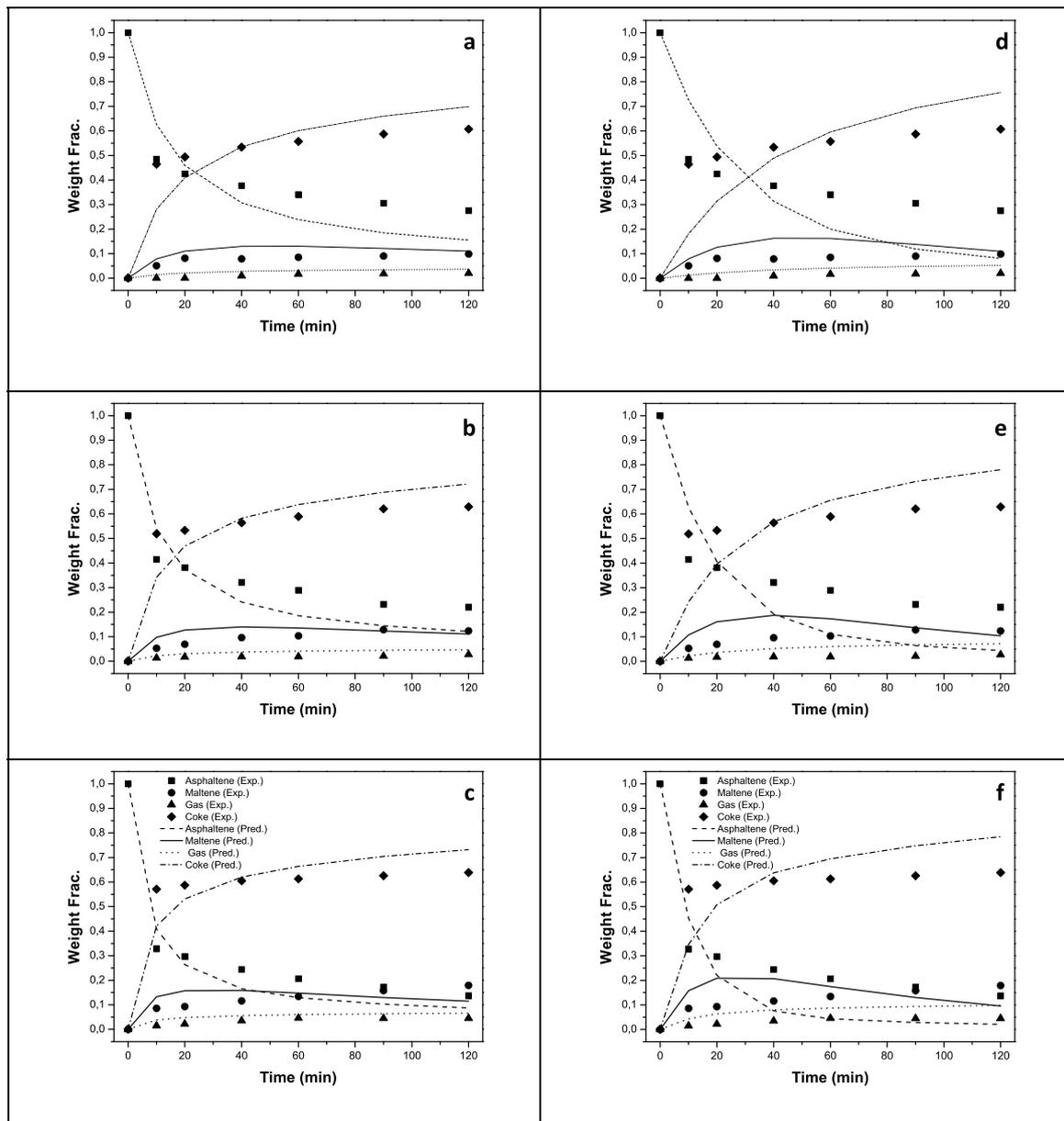


Figure 2: Comparison between experimental data and model prediction. (a: $n=2$ $m=2$ @350 °C, b: $n=2$ $m=2$ @375 °C, c: $n=2$ $m=2$ @400 °C and d: $n=1$ $m=1$ @350 °C, e: $n=1$ $m=1$ @375 °C f: $n=1$ $m=1$ @400 for Besikli asphaltene)

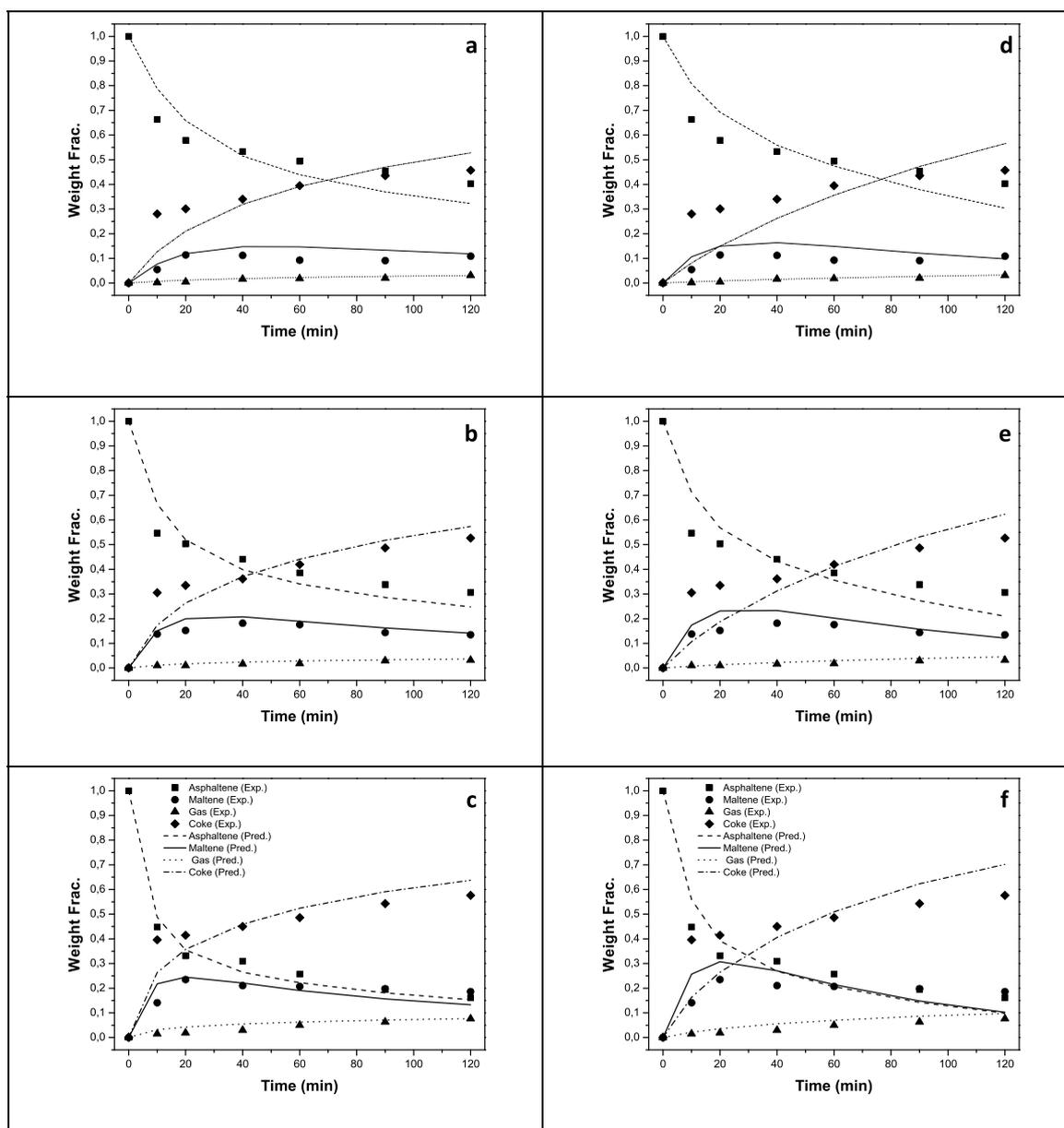


Figure 3: Comparison between experimental data and model prediction. (**a:** $n=2, m=2$ @ $350\text{ }^{\circ}\text{C}$, **b:** $n=2, m=2$ @ $375\text{ }^{\circ}\text{C}$, **c:** $n=2, m=2$ @ $400\text{ }^{\circ}\text{C}$ and **d:** $n=1, m=1$ @ $350\text{ }^{\circ}\text{C}$, **e:** $n=1, m=1$ @ $375\text{ }^{\circ}\text{C}$, **f:** $n=1, m=1$ @ $400\text{ }^{\circ}\text{C}$ for Garzan asphaltene)

Table 2: Estimated rate coefficients and R^2 values for each sample with different reaction orders.

Sample	Temp (°C)	Order of Reaction	k_1	k_2	k_3	k_4	k_5	R^2
BEŞİKLİ	350	n=2 m=2	0,7670	2,6903	0,1390	0,0000	3,2502	0,8026
	375		1,1087	3,8026	0,2447	0,0000	3,2502	0,8528
	400		2,0332	6,2084	0,5592	0,0000	3,2502	0,9027
	350	n=1 m=1	0,6063	1,2721	0,0885	0,0000	0,9421	0,4981
	375		0,8810	1,8203	0,1671	0,0000	0,9421	0,5937
	400		1,5063	3,0245	0,3781	0,0000	0,9421	0,7235
GARZAN	350	n=2 m=2	0,6116	0,9691	0,0556	0,0000	6,3896	0,7917
	375		1,4674	1,5753	0,1013	0,0000	6,3896	0,8995
	400		3,0586	3,3191	0,3985	0,0000	6,3896	0,9386
	350	n=1 m=1	0,9433	0,5470	0,0304	0,0044	3,3684	0,6539
	375		1,6597	0,7634	0,0507	0,0105	3,3982	0,7595
	400		2,8065	1,3185	0,1692	0,0183	3,4143	0,7880

Note: Unit of k values

n=1, m=1 case h^{-1} (k_{1-5})

n=2, m=2 case $wt. \text{frac}^{-1} h^{-1}$ (k_{1-5})

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