



# Particle-scale modeling of asphaltene pyrolysis in thermal plasma



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## ABSTRACT

Thermal plasma technique is proposed as a potential approach to pyrolyze asphaltenes to useful chemicals at ultrahigh temperature. Thermal plasma pyrolysis experiments show that acetylene is the major gaseous product with concentration up to 45 wt.%, together with some hydrogen and methane as well as the solids residue as by-products. To predict such a millisecond process, a particle-scale heat transfer model coupled with a modified competition kinetic model has been proposed, in which the heat exchange between the plasma gas and the particles as well as the heat transfer inside the particles are taken into account. Typical results indicate that the pyrolysis temperature would remarkably increase the heating rate. The heating rate would exceed  $10^7$  K/s at 2000 K in  $H_2$  thermal plasma and the devolatilization process would complete in 0.4 ms for 50  $\mu\text{m}$  asphaltene particles.  $H_2$  thermal plasma provides better heating exchange efficiency between the plasma and particles than He,  $N_2$  or Ar. Linear relationship is found between the heating rate and the devolatilization time under bi-logarithm coordinates at a certain temperature, regardless of the plasma gas compositions and pulverized sub-millimeter particle size, which gives powerful guidance for process optimization of the asphaltene pyrolysis.

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## 1. Introduction

Various upgrading methods [1–3] have been developed for the utilization of heavy crude oil [1] owing to the limited light crude oil resources. Solvent deasphalting method [3] is one of the techniques that upgrades crude oil to higher quality feedstock by separating the asphaltene and metals from the light components in the crude oil. The deasphalted oil (DAO) is employed as a lighter raw material to be further converted to valuable products by hydrogenation [4] or catalytic cracking [5]. Consequently, a large quantity of deoiled asphaltenes (DOAs) are generated at the same time as by-products [6]. However, those DOAs can be hardly transformed to valuable chemicals using conventional methods in petrochemical industry. Nowadays, efficient utilization of asphaltenes becomes crucial to improve the profit of the entire solvent deasphalting technology.

Generally, asphaltene contains more than 60 wt.% volatile matter, which makes it possible to acquire valuable products via thermochemical processes. Pyrolysis via thermal plasma has been developed as an alternative technology to convert various kinds of carbonaceous materials, including coal [7], tar [8] and paraffins [9]. Thermal plasma has the features of high enthalpy and high

temperature, and thus could realize efficient conversion of asphaltene to gas products and carbon black. Devolatilization is the first step of most thermochemical conversion processes, and is directly controlled by the heating conditions. Studying the devolatilization characteristics and particle heating history will benefit the understanding and optimization of the process. However, in thermal plasma pyrolysis, the heating rate reaches  $10^4$ – $10^7$  K/s [10], which is significantly different from traditional thermochemical processes (e.g.,  $10^2$ – $10^4$  K/s in combustion and gasification processes [11]). Owing to the extreme heating conditions, direct measurement of asphaltene particle behavior in thermal plasma reactor is difficult. Therefore, it is necessary to propose a model approach to theoretically analyze the heating procedure as well as the devolatilization process in detail.

In the present work, experiments of thermogravimetric analysis and thermal plasma pyrolysis were carried out to acquire the basic thermochemical properties of asphaltene firstly. Then a particle-scale model, coupled with the heat transfer model and the asphaltene devolatilization kinetic model, was introduced to investigate the pyrolysis behaviors of asphaltene under thermal plasma conditions. The heat exchange between the thermal plasma and the particle and the heat transfer inside the particles were considered. The effects of atmosphere temperature, plasma gas compositions and the particle size were discussed in detail. Further comparison

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was made to investigate the relationship between the heating rate and the devolatilization time.

## 2. Experimental

### 2.1. Asphaltene sample

The asphaltene particle sample, provided by Chinese University of Petroleum, was made by the spray granulation process [6,12]. The basic characterization analysis of the sample is shown in Table 1. The bulk density and porosity were measured by mercury porosimetry analysis (Micromeritics Corp., AutoPore IV 9500). The ultimate analysis was made via two elemental analyzers (PE Corp., PE-2400 II for oxygen test; EAI Corp., CE-440 for carbon and hydrogen test; Changsha Kaiyuan Instruments Co., Ltd., 5E-8S II for sulfur test). The proximate analysis was tested with a muffle furnace (CCRI, GW-300C) and a loft drier (Huamao Corp., DGF25012C) with the guidance of standard ASTM D7582-15. The size distribution of the sample particles was measured in a laser particle size analyzer (Malvern Corp., Mastersizer 2000).

### 2.2. Thermal plasma experiments

A 10-kilowatt (maximum) lab-scale device was used to carry out thermal plasma pyrolysis experiments of asphaltene. The device includes a plasma torch, a mixing section, a reaction chamber, a quenching section as well as a separator [7]. An insulated gate bipolar transistor (IGBT) rectifier power with a maximum output of 10 kW was used as the power source. The plasma torch consists of a cerium–tungsten cathode and a copper anode insulated with a PTFE pad. The working gases of plasma torch are Ar and H<sub>2</sub>. Asphaltene particles are delivered with a screw feeder and conveyed with Ar. The feedstock is then mixed with the plasma jet in the mixing section. Devolatilization takes place in the stainless-steel reaction chamber. To avoid secondary decomposition of product gas, additional Ar gas is fed into the quenching zone. Products then flow into the separation unit to separate the coke and carbon black from gas phase. Gas samples are collected to be further analyzed via an online mass spectrometer (AMETEK Corp., DCU 200) and two gas chromatography analyzers (Tianmei Corp., GC 7890-II; Shimadzu Corp., GC 2014). Light gases (including small molecule hydrocarbons and inorganic species like CO and H<sub>2</sub>) are analyzed respectively: CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are detected by GC-hydrogen flame ionization detector (FID) with a capillary column (HP-plot Al<sub>2</sub>O<sub>3</sub>, Agilent Corp.), while H<sub>2</sub>, Ar, CO and CO<sub>2</sub> are detected by GC-thermal conductivity detector (TCD) with a packed column (TDX-01, Lanzhou Chemical Engineering Research Institute).

**Table 1**  
Basic characterization analysis of asphaltene samples.

	Unit	Value
Bulk density (293 K)	g/cm <sup>3</sup>	1.37
Porosity	%	41.2
Volume average diameter	μm	55.6
Ultimate analysis (Md)	wt.%	
Carbon		88.0
Hydrogen		8.4
Oxygen		1.6
Nitrogen		1.6
Sulfur		0
Proximate analysis (Mar)	wt.%	
Volatile		66.7
Moisture		0
Fixed carbon		32.8
Ash		0.5

## 3. Mathematical model

### 3.1. Kinetic model

The established kinetic model to describe the asphaltene pyrolysis is mainly based on a two-step model [13]. However, this model has the disadvantage that the kinetic parameters should be refitted according to different heating conditions [13], and thus cannot be used to predict devolatilization behavior under unknown conditions. Instead of the two-step model, a modified competition model has been developed in the present work. The competition model, proposed by Kobayashi et al. [14], assumed that raw material pyrolysis process was governed by several first order competition reactions, and has been proved capable in describing the devolatilization of both coal [14] and biomass [15]. The first order assumption has also been proved successful in asphaltene kinetics investigation by Trejo et al. [16] and Ancheyta and Speight [17]. The mass loss rate and the volatile generation rate could be expressed as

$$dm = - \sum_{i=1,2,\dots} k_i m dt \quad (1)$$

$$dv = \sum_{i=1,2,\dots} c_i k_i m dt \quad (2)$$

$$k_i = A_i \exp\{-E_i/RT\} \quad (3)$$

where  $m$  and  $v$  represent the remained weight and generated volatile matter during pyrolysis, being function of time  $t$ ;  $c$  represents the volatile yield;  $k$  represents the reaction rate constant, and is described in the form of Arrhenius law;  $A$  and  $E$  represent the pre-exponential factor and activation energy.

It is widely accepted that the weight loss of asphaltene is mainly attributed to two clusters of reactions: the devolatilization of small molecule groups (methyl, ethyl, carboxyl, etc.) and the cracking reactions [18]. So, the number of the competing reactions in the present model is set as two to simplify the problem. On the other hand, original samples undergoes continuous changes in molecular structures during the pyrolysis process, which means the reactions are much easier to take place at the beginning and harder at the end of the devolatilization. So, a modification on the activation energy is added to reflect the effect:

$$E = f(E_0, \Delta E, m) = E_0 + \Delta E \times g(1 - m) \quad (4)$$

In Eq. (4),  $E$  is a function of initial value  $E_0$ , increment  $\Delta E$  and sample remaining mass fraction  $m$ ;  $g$  represents the modification function using '1 -  $m$ ' as a controlling variable, and is regressed from the thermogravimetric data. The parameters of the competition model can be fitted from thermogravimetric analysis at several different heating rates, and then further verified at extreme heating conditions. In thermogravimetric analysis, the standard error for TGA temperature reading is  $\pm 0.25$  K and for weight reading is  $\pm 10$  μg.

### 3.2. Heat transfer model inside a single particle

In the literature, it is usually assumed to be isothermal inside the particles. However, there is obvious temperature gradient inside the particles in thermal plasma pyrolysis, which would consequently affect the devolatilization process [10,19]. Therefore, it is important to employ a particle-scale model in order to investigate the heating procedure and the devolatilization process of asphaltene particles during thermal plasma pyrolysis. Some basic assumptions are made according to the process characteristics:

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