



# Behaviors of coking and stable radicals of a heavy oil during thermal reaction in sealed capillaries



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## HIGHLIGHTS

- Reaction of a heavy oil is studied in sealed capillaries at 250–500 °C.
- Mass and radical concentration of two types of cokes are quantified.
- The temperatures of these cokes' formation and transformation are reported.
- These cokes are characterized by radical concentration and line width of ESR.
- Activation energy of radical concentration is compared with that of coke formation.

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## ABSTRACT

This work studies thermal reaction of a heavy oil at temperatures of 250–500 °C in sealed capillaries. The samples are extracted by chlorobenzene and toluene, and the insoluble matters are quantified in mass and in radical concentration. It is found that the chlorobenzene insolubles (CI) forms at temperatures of and higher than 440 °C while the toluene insolubles (TI) forms at temperatures higher than 350 °C. Both of these insoluble matters increase with time and temperature, and approach to similar asymptotic values. The CI formation can be fitted with a combination of the second-order and autocatalytic kinetics while the TI formation can be fitted with the second-order kinetics. Both CI and TI contain stable radicals measurable by electron spin resonance (ESR), and the radical concentration in CI is higher than that in TI. The kinetics of stable radical concentration in CI and TI are different from that in mass, except that of TI at a low temperature range (350–440 °C). The changes in ESR line width of CI and TI are also studied. The above data are also discussed in terms of hard coke (CI insoluble matters) and soft coke (the difference between TI and CI), and in activation energy.

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## 1. Introduction

Efficient processing and utilization of heavy petroleum feeds are the focal points in petroleum refining. The technologies used for these processes, such as hydrogenation and delayed coking, are mainly carried out at temperatures of 350–500 °C. This temperature range allows thermal cleavage of some covalent bonds, such as C<sub>al</sub>-O, C<sub>al</sub>-S, C<sub>al</sub>-C<sub>al</sub> and C<sub>ar</sub>-C<sub>al</sub> bonds [1], to initiate a series of radical reactions including generation, propagation, coupling and condensation of reactive radical fragments. Coupling and condensation of the reactive radical fragments lead to the formation of heavy products that are heavier than the feed. The heavy products

may undergo dehydrogenation to form coke [2], which is responsible for poor product quality, deactivation of catalyst, as well as equipment fouling [3,4].

Coke is a generic name of heavy compounds with complex composition and structures. It is commonly defined as the insoluble matters in some organic solvents such as toluene. The toluene insoluble coke, however, can be further classified into soluble and insoluble fractions in some strong solvents such as quinoline, chlorobenzene or a mixture of pyridine and carbon disulfide, as systematically studied by Wiehe who proposed a two-dimensional solubility parameter to characterize the solvent power [5,6]. Depending on the dissolution capacities of solvents, the fractions insoluble in a strong solvent may be termed as hard coke (HC) while those soluble in a strong solvent but insoluble in a weak solvent may be termed as soft coke (SC). For examples, Sahoo et al. defined the dichloromethane soluble fraction of the

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coke deposited on hydroprocessing catalysts as soft coke while the dichloromethane insoluble fraction of the coke as hard coke [7,8]. Koon et al. used chloroform to classify the coke deposited on fluid catalytic cracking (FCC) catalysts into soft coke and hard coke [9]. Although this classification of coke components was found useful to understand transformation of coke during thermal and catalytic reactions, kinetics of the coke formation was very limited in the literature.

It is recognized that a longer reaction time and a higher temperature promote coke formation [10]. Removing the olefins from a feed or reducing the liquid-side transport resistance between fluid coke particles and the heavy feed can both inhibit coke formation [11–13]. This information, though useful in addressing operation requirements, shows limited understanding on the fundamental radical reactions, especially on the behavior of the radicals measurable by electron spin resonance (ESR).

ESR has been used to study radical behaviors in pyrolysis or liquefaction of coal and biomass for decades. However, the nature of ESR radicals was not clear. These radicals were assumed to be the active ones or a sum of the active and stable ones in many studies, and their concentrations were even incorporated in kinetics of coal liquefaction as independent variables [14]. This understanding, however, was proven to be incorrect. Petrakis et al. showed that the radical concentration measured in-situ at the reaction temperatures (450 °C) in coal pyrolysis is the same as that measured at the ambient temperature [15]. Liu et al. showed that in biomass pyrolysis experiments, the active radicals captured by the H donated from 9,10-dihydrophenanthrene are three magnitudes of that measured by ESR [16]. In principle, detection of the active radicals by ESR is not possible, because most of the radical reactions are very fast, in nanoseconds, while the response time of ESR is much longer, in microseconds.

It has been recently reported that the radicals measured by ESR are the stable ones, and the term “stable” does not mean that they are chemically inactive, but rather they are confined in structures that allow little access to other radicals [17]. He et al. showed that the tars derived from pyrolysis of coal and biomass contained stable radicals, and these radicals were mainly in coke defined as tetrahydrofuran (THF) insolubles [17–19]. Furthermore, the stable radical concentration of biomass tars generated from a fixed-bed reactor under an inert gas purging started to increase at temperatures higher than 300 °C, while that of coal tars started to increase at temperatures higher than 350 °C. These behaviors were attributed to the cracking of tars and the condensation of large radical fragments to form coke. The radical concentrations were as high as 10 μmol/g at 450 °C in 30 min. Retcofsky et al. reported that the stable radical concentration and ESR line width of coal-derived oils, asphaltenes and preasphaltenes are different [20]. The ESR line width of coals decreased with increasing coal rank, especially in a carbon content range of 80–93%, due to significant increases in coal's aromaticity at higher carbon contents [21]. This change in ESR line width in coals was confirmed by Kwan et al. and explained by the formation of larger condensed aromatic rings [22]. Meinhold et al. showed that when the coke in the HZSM-5 channel condensed to form polycyclic aromatics, its line width significantly decreased [23]. Singer et al. concluded that a narrower line width contributes to a stronger aromaticity because the acenaphthylene pitch which contains no alkyl substituted aromatic components, showed a narrower line width than petroleum pitch and ethylene pitch [24]. All the information presented above suggests that the ESR data can be used to characterize the changes in coke content and property during thermal reaction of heavy oil fractions.

This paper studies coking and stable radical behaviors of a heavy oil during thermal reaction in a temperature range of 250–500 °C. The coke is defined in two sub-fractions, insoluble in

chlorobenzene and insoluble in toluene, to meet the need of a particular purpose. Kinetics of the coke formation and stable radical concentration are also developed and compared.

## 2. Experimental

### 2.1. The physical property and composition of the heavy oil

The heavy oil, termed oil in short, is a synthetic oil provided by ExxonMobil Chemical Company. It is a viscous black liquid at room temperature with a relative density of 1.06–1.10, a flash point of 102 °C (ASTM D-93), an autoignition temperature of 550 °C and a boiling point range of 218–649 °C. It contains 80.3% aromatic carbon, 19.7% aliphatic carbon, <5.0 wt% anthracene, <5.0 wt% phenanthrene, <0.1 wt% naphthalene and >0.1 wt% polynuclear aromatic hydrocarbons. It is low in H content and contains initially 89.9 wt% heptane insoluble, 2.0 wt% toluene insolubles and 4.0 wt% chlorobenzene insoluble as shown in Table 1.

### 2.2. Thermal reaction of the oil

The oil was heated to 100 °C in an oven and maintained for 1 h before being sampled with capillaries of 1.1 mm in diameter. Each of the capillaries loaded with  $5.5 \pm 1$  mg oil was placed into a glass tube of  $\phi 2 \times 30$  mm and sealed by a burner after being purged with N<sub>2</sub> for 15 s to eliminate the influence of oxygen on the radical reaction and ESR measurement [25]. The procedure is graphically shown in Fig. 1.

The thermal reaction of oil was carried out in a thermostat with 20 slots. The glass tubes sealed with oil were inserted into the slots maintained at a temperature of 250, 300, 350, 400, 420, 440, 460, 480 or 500 °C. One of the glass tubes was taken out of the slot and cooled in air after being maintained at a temperature for 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 7.5, 10.0, 15.0, 20.0, 30.0 or 40.0 min. The sample reached 350 °C in less than 0.5 min for the set temperatures of 420–500 °C and reached the set temperatures in less than 2 min as shown in Fig. S1. The temperature fluctuation of the thermostat was less than 1 °C.

The cooled glass tubes were directly loaded into an ESR unit for radical concentration measurement. The glass tubes were then cut open at the top and fully immersed in 0.5 mL chlorobenzene or toluene in a test tube for 48 h. The solvent to sample ratio was about 90:1 in mL:g. The solvent with soluble fractions was then removed from the test tube and the insoluble fraction was washed with 0.1 mL fresh solvent two times by pipetting. The insoluble fraction in the tube was dried in a vacuum oven at 50 °C for 24 h and then subjected to ESR measurement. The glass tube with the insoluble fraction was subjected to combustion in air at 450 °C for 6 h and the mass difference between the glass tube with and without the insoluble fraction is the mass of insoluble fraction.

Some of the toluene insoluble fraction (TI) is soluble in chlorobenzene, 30 wt% in some cases, for example [26]. This indicates that the chlorobenzene insoluble fraction (CI) is heavier than TI. Based on this information, the CI is termed hard coke while the TI is termed hard + soft coke, and consequently the difference between TI and CI is termed soft coke.

### 2.3. ESR measurement

The ESR spectrometer used is JES FA 200 (JEOL, Japan). The samples were measured at room temperature and the results were calibrated by 2,2-diphenyl-1-picrylhydrazyl (DPPH). The capillaries and the glass tubes showed little influence on the samples' ESR results.

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