

# RHEOLOGY AND KINETICS OF COKE FORMATION EVALUATED USING A SIMPLE, HIGH PRESSURE VISCOMETER

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## Introduction

Although coke formation often is described as a chemical process involving free radical combination reactions, it is primarily a physical process -- the stretching and alignment of mesophase by percolation of gas -- which impacts the suitability of coke in high-severity electrode applications. To understand better, therefore, the physical changes which accompany formation of coke, feedstock viscosity was followed to levels as high as 3 million cp using a specially-designed high-temperature, high-pressure viscometer.

## Experimental

The apparatus used for our viscometry experiments is shown in Figure 1. It consists of a hinged, electrically-heated 5-inch diameter aluminum block which can be moved to surround a 1½" diameter reactor tube containing the coker feedstock and a viscometer probe. Viscous resistance of the reactor fluid is measured with a Nametre viscometer by the electrical power required to maintain a constant amplitude of oscillation in a 5" probe connected to a transducer. By containing the fluid in a heated pressure vessel (batch coker tube) surrounding the probe, we are able to measure viscosity at any pressure up to the MAWP of the reactor vessel.

At the highest feedstock viscosity measurable by our viscometer, 3 million cp, conversion of feedstock to coke is well underway. For material collected in the vicinity of the tip of the viscometer probe, Figure 2 shows that viscosity of 3 million cp corresponds to roughly a 90% mesophase content in the pyrolyzing feed.

## Results and Discussion

It is well known that a change of coking temperature dramatically impacts coking kinetics. Temperature also impacts the longevity of the fluid mesophase. Figure 3 shows, for example, that at 911°F a typical needle coker feedstock remains between

$1.0 \times 10^4$  and  $3.5 \times 10^6$  cp (or, from Figure 2, between 75 and 90% mesophase) for 31 minutes. This compares to 168 minutes at 856°F.

A change of feedstock can impact the overall time of fluidity but, unlike a change of coking temperature, feedstock has a much smaller impact upon the time within the high-mesophase-content regime. Figure 4 shows, for example, virtually parallel lines of viscosity versus reaction time for a decant oil which was hydrotreated at three different severities. Even heavy premium gas oil, which initially is far less reactive than a typical coker feed, spends similar time in the high-viscosity, high-mesophase content regime.

It has been shown that the logarithm of feedstock viscosity is proportional to feedstock molecular weight. Actual molecular growth rates, therefore, can be quantified by fitting logarithmic viscosity data obtained in this investigation to a first order kinetics expression. Rate constants presented in Figure 5 confirm that, for feeds with a wide range of properties, molecular growth rates in the high-viscosity regime ( $>1 \times 10^4$  cp) are remarkably similar.

Because the coker feed is well known to impact coke macrostructure, these results suggest, in general, that fluidity at lower levels of viscosity ( $<1 \times 10^4$  cp) may influence coke macrostructure as much or more than fluidity characteristics at higher levels of viscosity. Calculations from Stokes Law demonstrate, in fact, that single gas bubbles greater than about 0.5 mm diameter likely will not rise at an appreciable rate when the feedstock viscosity is greater than approximately  $5 \times 10^3$  cp.

## Conclusions

A simple viscosity apparatus is shown to allow measurement of physical transformation relatively far into the coke-making process. Contrary to the accepted view that coking rate is sensitive to the coker feed, this study demonstrates that--at relatively high levels of viscosity--a number of widely-differing coker feeds have remarkably similar rates of molecular growth.

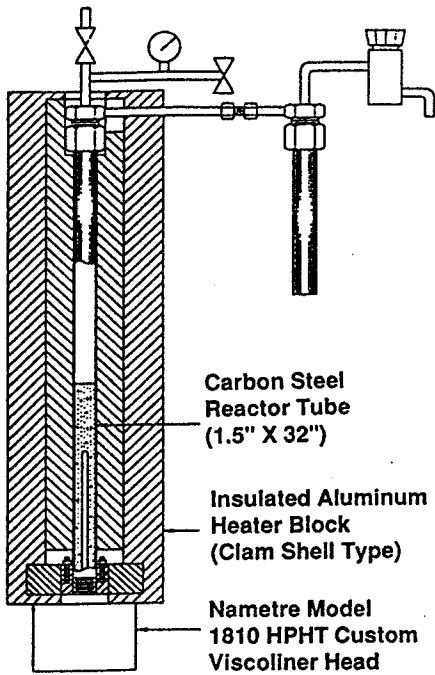


Figure 1. High pressure/high temperature viscosity apparatus

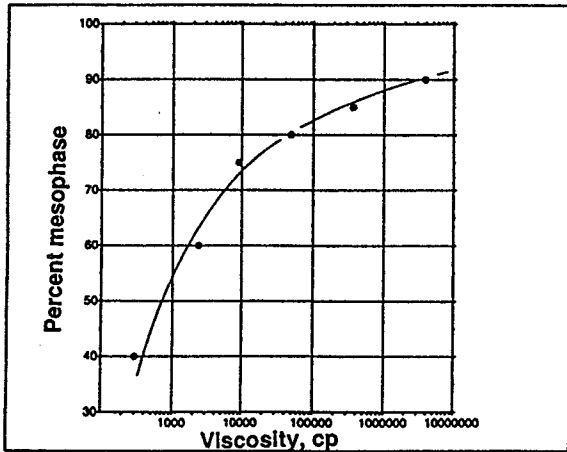


Figure 2. Mesophase content vs. viscosity of a typical feed coked at 858 deg F and 60 PSIG

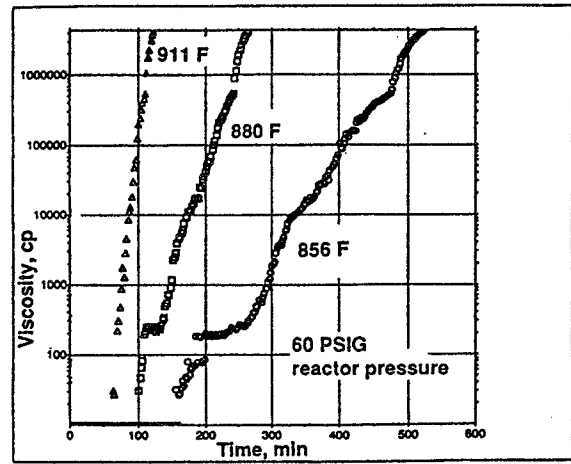


Figure 3. The effect of time and temperature on viscosity from a typical coker feed

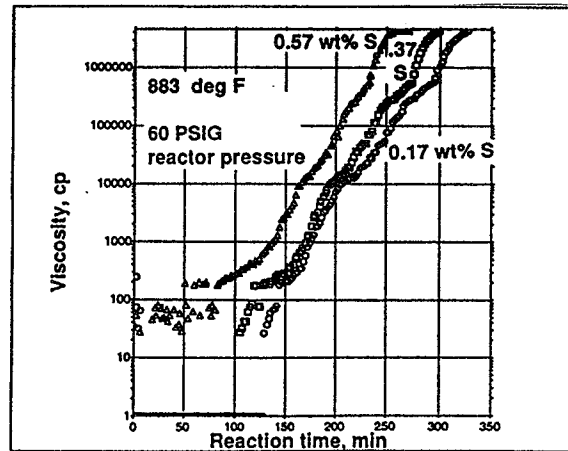
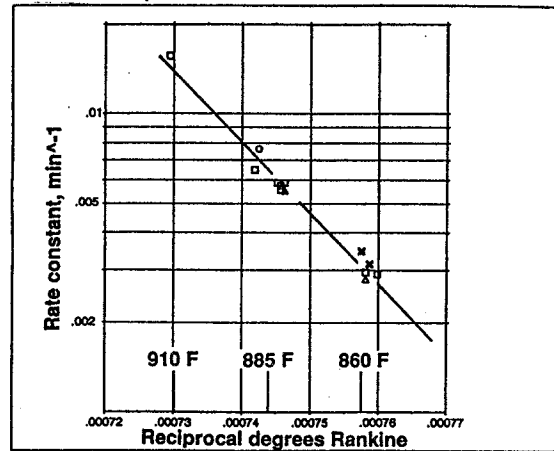


Figure 4. Viscosity vs. reaction time for a decant oil hydrotreated at different severities



- Coker feed a,  $f_a = 73.2$  (0 PSIG)
- Coker feed a,  $f_a = 73.2$  (60 PSIG)
- ▲ Coker feed b,  $f_a = 56.2$  (60 PSIG)
- ✖ Coker feed c,  $f_a = 52.6$  (60 PSIG)
- ▲ Coker feed d,  $f_a = 83.1$  (60 PSIG)

Figure 5. First order rate constants obtained from viscosity data