Chemical mechanism for the formation of coke from the pyrolysis of a heavy Colombian crude oil

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This study reports experiments to study the pyrolysis of maltenes and asphaltenes from a Colombian heavy crude oil, using an horizontal furnace, in an inert atmosphere, at a low heating rate (2 °C/min) and at 300°C, 350°C, 400°C and 450°C. Oil from Castilla well was used in the experiments, as well as, maltenes and asphaltenes separated from this oil. The Castilla Oil has a density of 0.98 g/cc at 15°C (13.4 API) and a viscosity of 971.9 cSt at 50°C. Asphaltenes and maltenes were separated from Castilla oil according to the ASTM D-6560 method. The hydrocarbons were mixed with Ottawa sand (with a size range of 250 µm-500 µm).

The experiments were carried out in a 2.54-cm ID horizontal furnace in which the mixture of 80%wt Ottawa sand and 20% hydrocarbons (crude oil, maltenes or asphaltenes) reacted in a nitrogen atmosphere at a heating rate of 2°C/min up to the final temperature. The nitrogen flow was varied from 1153.4 scm^3/min to 1455.3 scm^3/min to guarantee a constant superficial velocity during the constant temperature stage. The reactor, made of stainless steel 304, was cooled down to atmospheric temperature at a rate of 19°C/min to stop the pyrolysis reactions. The condensable fraction, named as LMWM (low molecular weight maltenes) was collected in a cold trap set at -20°C, the residue in the furnace was further separated in maltenes, asphaltenes and coke. The non-condensables were estimated from the mass balance difference. Quantification of maltenes and asphaltenes in the furnace residue was by the standard method IP-469. Coke was quantified as the fraction insoluble in toluene.

Figure 1 shows the variation of the different fractions with temperature during the pyrolysis of maltenes. At 300 °C the mass fraction of maltenes is 0.49 g_m/g_{tot} whereas that for gas is as high as 0.38 g_g/g_{tot}. The concentration of maltenes decreases down to 0.11 g_m/g_{tot} at 450°C as the amount of LMWM increased from 0.09 g_{LMWM}/g_{tot} up to 0.31 $g_{LMWM}/g_{tot.}$ Clearly, as temperature increases, maltenes crack to form low molecular-weight species.

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During the thermal cracking of maltenes, the production of asphaltenes is low and only becomes important at 400°C. Coke was only measured at 450°C.

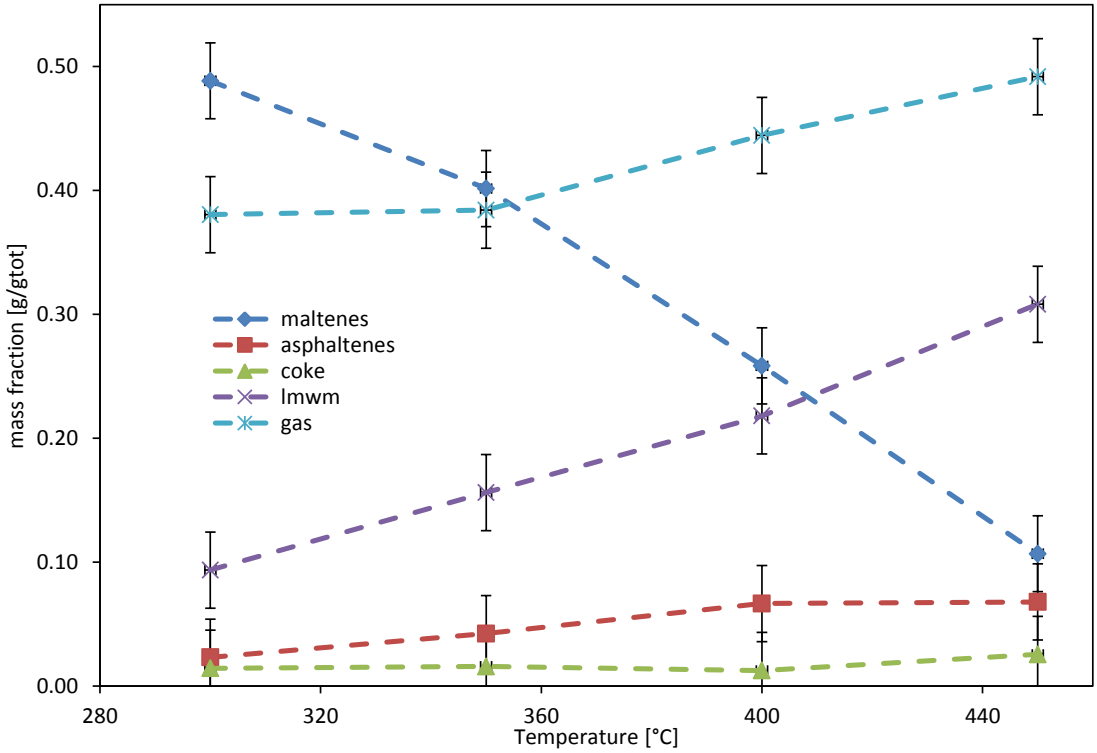


Figure 1. Variation of the concentration of the different fractions during the pyrolysis of maltenes

Figure 2 shows the variation in the concentration during the pyrolysis of asphaltenes. As the concentration of asphaltenes decreased from 0.46 g_a/g_{tot} at 300°C down to 0.18 g_a/g_{tot} at 450°C, that of maltenes increases from 0.26 g_m/g_{tot} at 300°C up to 0.46 g_m/g_{tot} at 400°C. Meanwhile the fraction of LMWM increased from 0.26 g_{LMWM}/g_{tot} up to 0.29 g_{LMWM}/g_{tot} in the same temperature range. This tendency suggests that at temperatures below 400°C asphaltenes mainly react to form lower molecular weight fractions such as maltenes and LMWM. At higher temperatures the pyrolysis of asphaltenes yields coke and gas.

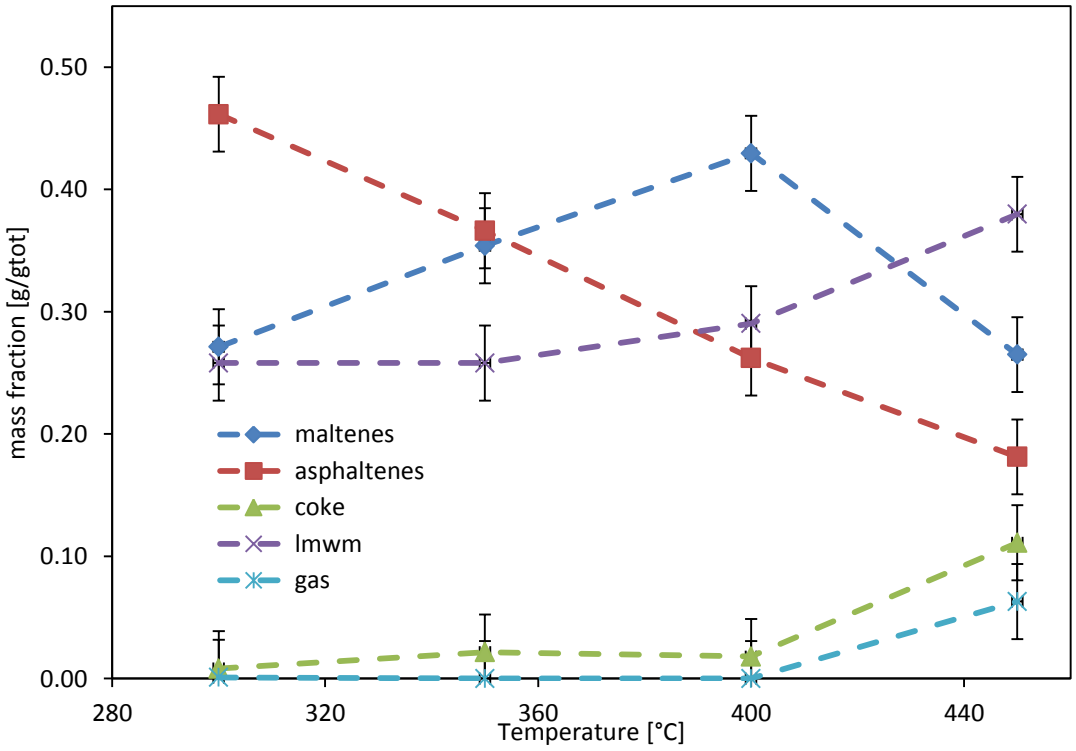


Figure 2. Variation of the concentration of the different fractions during the pyrolysis of asphaltenes.

Figure 3 compares the amount of coke formed during the pyrolysis of maltenes, asphaltenes and crude oil as well as that calculated when the fraction of coke formed by maltenes and asphaltenes is added based on the concentration of these fractions in the original crude sample. Coke from asphaltenes is higher than coke from maltenes while coke from crude oil has an intermediate value. The experimental and calculated values of coke agree well which suggest that the coke formed from crude oil can be calculated as the combination of the independent crude oil fractions.

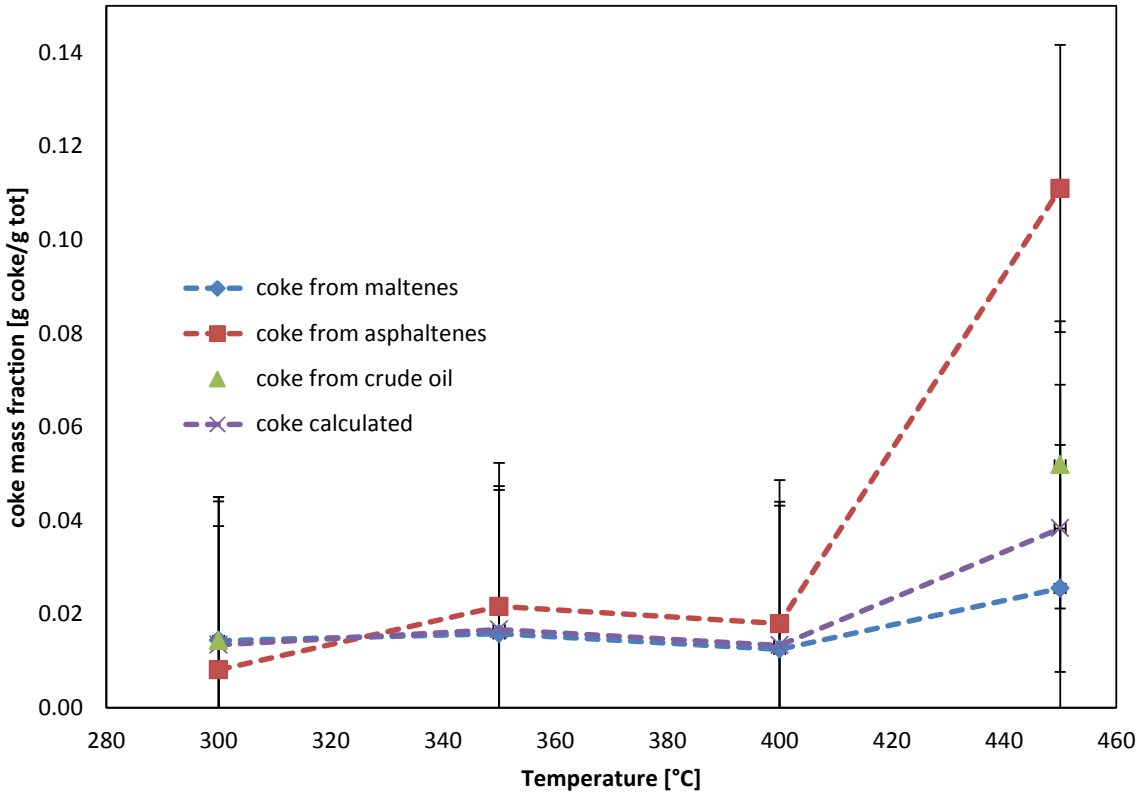


Figure 3. Comparison of coke formation during the pyrolysis of maltenes, asphaltenes, and crude oil.

The figure shows the results when the coke fraction is calculated as a linear combination of that formed from the pyrolysis of maltenes and asphaltenes.

Given the complexity of crude oil, a reaction mechanism based on actual chemical species that describe coke formation during the pyrolysis of oil would be a very difficult ordeal. The alternative taken by the petroleum industry is to use pseudo-components. A similar approach is taken in this research. The emphasis, however, was given to improve the chemical understanding of the coke-formation process.

To propose the reaction mechanism, we took into consideration that during the pyrolysis of heavy crude oil, both high- and low-molecular-weight molecules (maltenes and asphaltenes) undergo thermal cracking and form radicals. Reaction between these radicals produces low-molecular-weight molecules that can be condensable or non-condensable gases. Addition of these radicals to high-molecular-weight molecules, promotes growth and eventually, through physical condensation, a coke precursor is formed. This coke precursor grows to form coke as a result of the addition of low-

molecular-weight aromatic radicals and unsaturated molecules and the continuous physical condensation of high-molecular weight molecules.

A reaction mechanism that captures this chemistry, considering the formation of both high- and low- molecular weight fractions from an original fractions, and taking into account the experimental results in which after thermal cracking of maltenes and asphaltenes there were also condensable, non-condensable gases and coke, it is the one in Figure 4 that schematically represents reactions 1 and 2.

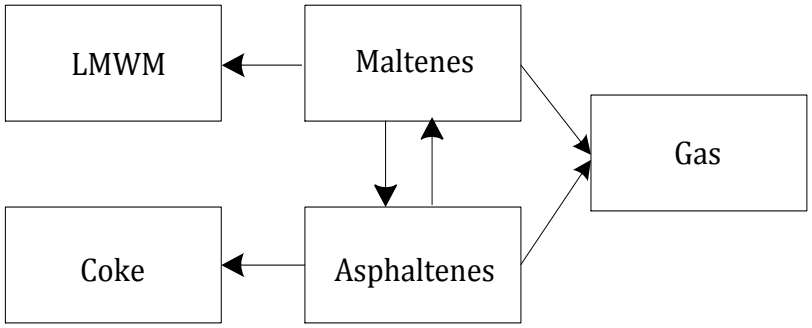


Figure 4. Reaction mechanism scheme

$$\text{Maltenes} \longrightarrow \text{Asphaltenes} + \text{LMWM} + \text{gas} \qquad (1)$$

$$\text{Asphaltenes} \longrightarrow \text{Maltenes} + \text{coke} + \text{gas} \qquad (2)$$

This reaction mechanism considers that coke only comes from asphaltenes, nonetheless maltenes also contribute to the final coke formation because of the thermal cracking reactions that allow the conversion of maltenes to asphaltenes and that after more thermal cracking process form coke. It is important to highlight that crude oil fractions not only go to heavier fractions, as is usually reported for crude oil pyrolysis reaction mechanisms. For this reason we consider the formation of maltenes from asphaltenes, lmwm from maltenes and gas from maltenes and asphaltenes.

Key words: coke formation, crude oil fractions, pyrolysis, in situ combustion.