

Adsorption Kinetics Studies Of Heavy Hydrocarbons Over Adsorbent and Catalysts.

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Introduction

Heavy oil and bitumen are likely to be among the dominant fossil fuels available as energy sources during the next several decades [1]. The “tar sands” of western Canada are prominent among these. Data indicate that surpluses of vacuum residue (VR) derived from upgrading operations are expected to occur. New upgrading schemes must be developed in order to economically and environmentally manage this VR accumulation. Our research group is developing techniques for VR upgrading that include the modification of the feed by combining mild thermal cracking [2] followed by adsorption of the modified heavy molecules over tailor-designed adsorbents and or catalysts and finally catalytic steam gasification of the adsorbates for hydrogen production [3]. Understanding the adsorption phenomena is of utmost importance in this work. Both kinetic and uptake results over different solids, have been obtained after different degrees of visbreaking. This paper will present adsorption results obtained with asphaltene fractions isolated from virgin and visbroken products. Solids examined include macroporous kaolin, a catalyst derivative of this, clay minerals and a real sample from Athabasca reservoir. The adsorption behavior of these solids and preliminary correlations established among adsorption phenomena and adsorbate properties are discussed.

Materials and Methods

Different solids were employed in this work. Macroporous kaolin was prepared to have desired macropore proportions (average diameter greater than 50 nm). The preparation uses kaolin as the primary component and is then calcined up to 650 °C for 8 hrs. Clay minerals used include a Ca-Montmorillonite (from Apache County, Arizona, USA) and a Na-Montmorillonite (from Crook County, Wyoming, USA). A representative sample from an Athabasca siltstone (well 88-14-27, 11W4 at a depth of 282.2 m) was also utilized. Samples were characterized using the BET method with a CHEMBET-3000 unit from Quantachrome Instruments and a mercury porosimetry. Each sample was dried at 150 °C prior adsorption experiments and stored in desiccators prior to use. Visbreaking of the Athabasca vacuum residue was carried out at 380 °C. Reaction times were varied to allow collection of visbroken products (VB) with diverse conversion levels, up to 35 wt %. Experiments were terminated after the desired pre-calculated amounts of distillates were collected. The adsorption studies were performed using a fixed sample concentration (~60 ppm) in a toluene solution. Adsorption studies for sample solutions were carried out by ultraviolet-visible spectroscopy (Uv-Vis). The adsorption kinetics of the solids were determined at 295 K and the residence time for the adsorption experiments was 6 hrs.

Results and Discussion

The adsorption kinetics were determined for each asphaltene fraction over the selected clay minerals, over one particular catalyst based on macroporous kaolin and the Athabasca siltstone. In all experiments, absorbance was normalized (absorbance at time t / initial absorbance) vs. time (min) in order to make it independent of the initial concentration. Typical errors in the absorbance scale do not exceed 10 % relative.

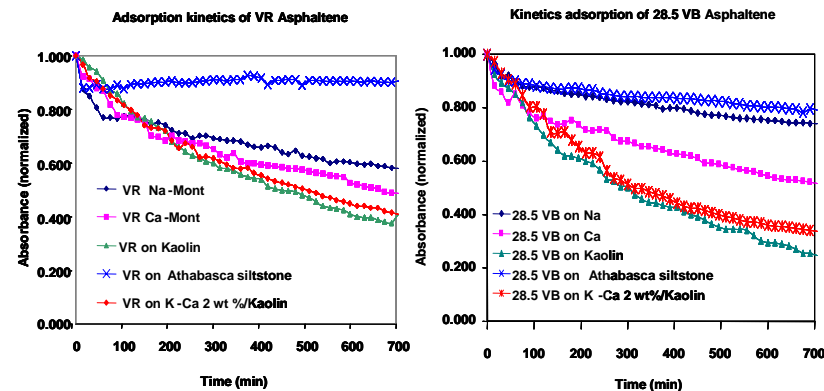


Figure 1. Adsorption kinetics of the precipitated asphaltene from VB products at 293 K: (a) VR asphaltene (b) 28.5 conversion, VB asphaltene.

The different adsorption behaviours for the VR asphaltene and 28.5 conversion VB asphaltene over the solids and catalyst are displayed in Figure 1a and 1b. The clay minerals have a higher uptake of the VR asphaltene during the initial stages of the adsorption (less than 60 minutes). The macroporous kaolin, the kaolin catalyst and Ca-montmorillonite display higher uptake with continued adsorption. The sample of Athabasca siltstone did not show adsorptive capacity with this VR fraction. Higher uptake is observed during adsorption for the macroporous kaolin, the catalyst derivative of it and Ca-montmorillonite clay with respect to the 28.5 VB asphaltene. The Na-montmorillonite and the Athabasca siltstone showed the poorest adsorption. The results above indicate that the nature of the asphaltene samples along with the intrinsic nature of the solids govern the adsorption.

References

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