

ADSORPTION STUDIES OF VIRGIN AND THERMAL CRACKED RESIDUA OVER AN ATHABASCA CORE SAMPLE.

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Introduction

Decline in conventional crude oil reserves has promoted an increase in the need to exploit heavy oil and bitumen. These are likely to be among the dominant fossil fuel energy sources during the next decades. Abundant Oil Sands in Northern Alberta are one of the most suitable sources of future oil supply. Development of cost effective, environmentally sensitive upgrading schemes for heavy hydrocarbon reserves is a must due to the intrinsic nature of heavy oil and bitumen. Particularly, inside the current research activities performed in the Alberta Ingenuity Centre for In Situ Energy (AICISE), new upgrading initiatives under study¹⁻³, include Catalytic In Situ Upgrading (CISU) which has the potential to be a more environmentally and economically efficient bitumen processing than conventional surface upgrading. During CISU, mild thermal cracking is expected to affect bitumen to some level, thus producing cracked products within the reservoir and, leaving environmentally undesirable components within. The large proportion of mineral matter in the reservoir plus its inherent heterogeneity is expected to induce adsorption phenomena over such reactants and products. Therefore, it is necessary to assess the extent of the adsorption phenomena aiming at a better understanding of the upgrading and recovery efficiency of hydrocarbons from the reservoir.

Here we present some aspects of our research related to the adsorption uptake and kinetics of interaction between heavy molecules (vacuum residue from Northern Alberta bitumen and its thermal cracked products) and core samples from an Athabasca reservoir (well 14-27-88 11W4; depth from 264 m to 308 m). The adsorption measurements are carried out with toluene solutions of virgin and thermally cracked Athabasca vacuum residue. Two visbroken products (mild thermally cracked) were selected as proxies for the expected materials remaining within partially depleted reservoirs exposed to thermal treatments¹.

Correlations among adsorption uptake with adsorbents i.e., minerals and product properties are discussed. Insights into surface characteristics that may control on adsorption phenomena are presented.

Experimental

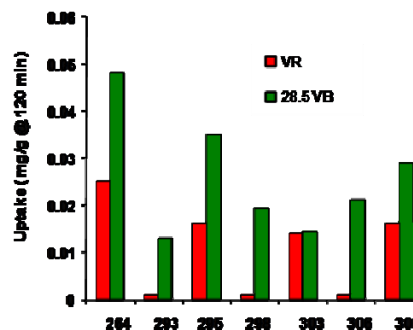
Toluene (Spectrophotometric Grade), methylene chloride and n-heptanes (HPLC grade) from Sigma-Aldrich were used as received. A vacuum residue from Athabasca bitumen provided by Suncor was employed in this work. This feedstock contains 26 wt % distillable fractions (545°C-) as determined by gas chromatography simulated distillation (SimDist). About 0.7 wt % insoluble materials was determined to be present within the sample using methylene chloride. Visbroken residues (obtained through a mild thermal cracking process) at different conversion levels were prepared according to a previous report⁵. Seven samples from an Athabasca core (well 14-27-88 11W4; depth from 264 m to 308 m) were selected and cleaned of bitumen via soxhlet extraction with dichloromethane. Samples are

referred to by depth. Bitumen from the selected layers was removed via soxhlet extraction with DCM. Dichloromethane extracts were submitted to further characterization while mineral portions were dried at 373 K before performing the adsorption experiments. For the adsorption experiments, the methodology employed has been previously reported⁶. Typically, dried minerals in powder form were contacted with toluene solutions of the VR feedstock and VB product, keeping a sample/adsorbent ratio of 10 (w/w). Solutions concentration was 60-70 ppm w/vol. In all experiments, the absorbance $A(t)$ was converted in relative absorbance $RA(t)$ (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.

Results and discussion

Adsorption experiments with Athabasca core samples were carried out in order to estimate the adsorptive capacity of the sand as a function of depth and minerals composition. The Athabasca core is extremely heterogeneous, containing intervals of siltstone interbedded with bitumen saturated sand. Some sections of the core contain inter-layered quartz sand and siltstone on millimetre scale; other intervals contain several metres of bitumen saturated quartz rich sand. The top of the core is characterized by Glauconitic sand and shale.

Toluene solutions of VR and one visbroken product produced at the highest severity before solids precipitate (28.5 VB) were used to incorporate the adsorbates into the media. Adsorption experiments were performed under the conditions described in the experimental section, being adsorption uptakes at 120 min presented in Figure 1.



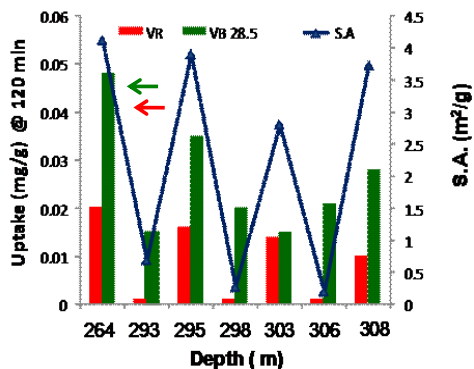
Conditions: solid=0.3 g, adsorbate=3ml, C₀=60-70 ppm, T=295 K, t=2 h, solution/adsorbent= 10

Figure 1. Uptake (mg/g) at 120 min for VR and 28.5 VB over Athabasca core samples studied (sample numbers correspond to depth in core)

Different uptakes were obtained along the depth of the core as presented in figure 1. This is particularly true for VR, samples from 264, 295, 303 and 308 metres show higher uptake in comparison with the rest of the samples. The 264 metre sample, which is at the top of this core, consists of glauconitic sand, glauconite is a mica group mineral with a formula: $(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$. Samples from 293, 298 and 306 meters are composed by quartz rich sand, and thus show the poorest uptake. Samples from 295, 303 and 308 meters contain mm-scale inter-layers of quartz sand and siltstone; the proportion of quartz in these samples is lower than in the quartz sand and they have a higher uptake. On these samples the uptake is clearly a function of the minerals present.

Now considering adsorption for the 28.5 VB sample, it is easily observed (Fig. 1) how for all the studied cases this sample displays more affinity to the surfaces. Once again, the 264 sample showed the highest adsorption. As expected from published literature on thermal conversion processes, large molecules present in VR cleaved into smaller molecules depending on the severity of the process⁸. It means that with increased thermal conversion, larger amounts of low molecular size compounds are produced, increasing the possibility for larger uptakes into the porous space of solid sorbents. Indeed, we determined the MM's of the studied residua by Size Exclusion Chromatography (SEC) in *ortho*-dichlorobenzene and the obtained values, VR (1459 Da) and 28.5 VB (689 Da) support the above statement.

Correlations between the uptakes obtained for both adsorbates with the surface areas are presented in Figure 2.

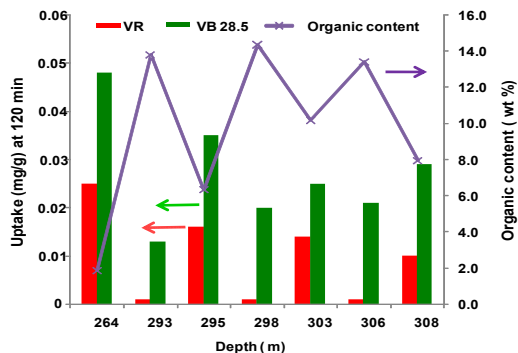


Conditions: solid=0.3 g, adsorbate=3ml, C0:=60-70 ppm, T=295 K, t=2 h, solution/adsorbent= 10

Figure 2. Uptake (mg/g) at 120 min for VR and 28.5 VB over Athabasca core samples vs. surface area (m²/g)

The findings presented in Figure 2 suggest that surface area is a parameter that impacts adsorption. It is more noticeable for VR, i.e., the higher uptakes were achieved with materials having surface areas higher than 2 m²/g. For 28.5 VB adsorption, minerals with high surface area help, but the adsorption is not limited by this parameter. It seems that other factors could drive the adsorption, such as aromaticity and/or heteroatom contents, in a similar way as observed recently for Athabasca-C₇-Asphaltene⁶. This indicates that the adsorption may depend on specificities of the molecules being adsorbed.

Correlation between the uptakes obtained for both adsorbates with the initial organic content present in the sample is shown in Figure 3.



Conditions: solid=0.3 g, adsorbate=3ml, C0:=60-70 ppm, T=295 K, t=2 h, solution/adsorbent= 10

Figure 3. Uptake (mg/g) at 120 min for VR and 28.5 VB over Athabasca core samples vs. organic content (wt %)

Samples that contain initially lower organic amounts, display higher uptakes. This can be due to: 1. the fact that this organic matter could cover all of the accessible sites available for the adsorption in these particular layers, 2. non-adsorbing quartz rich layers function only as traps for organic matter, 3. that the fine-grained nature of the siltstone in these samples did not allow them to be fully charged with oil.

For the more adsorptive mineral samples, adsorption kinetics were followed for 120 minutes in experiments using toluene solutions of virgin (VR) and thermally cracked product (28.5 VB). The kinetic analysis was restricted to the linear portion that occurs within the first 60 minutes of the experiments. The values were fitted to a first order kinetic equation to determine kinetic coefficients⁶. The values found are presented in Table 1.

Table 1. Apparent First Order Rate Constant for the Adsorption of VR and 28.5 Visbroken Product Over Core Samples After 120 Min

Sample	K x10 ³ min ⁻¹	
	VR	28.5 VB
264	1.2 ± 0.3	2.3 ± 0.3
295	0.9 ± 0.2	1.6 ± 0.2
303	0.8 ± 0.2	0.9 ± 0.2
308	1.0 ± 0.2	1.2 ± 0.3

As shown in Table 1, at the initial stages VR adsorption was faster on the sample 264 followed by sample 308. Adsorption kinetics for this adsorbate was found nearly constant for the other 2 studied minerals. After thermal cracking (28.5 VB), drastic increases in kinetic coefficients were determined for mineral samples 264 and 295, meaning that the cracked products display increased affinity for those surfaces. As mentioned before, the presence of certain types and quantity of minerals on such samples could be the driving force for the adsorption. This point will be covered in an ensuing section. Herein, to get further insights on possible effects derived from heteroatom contents present in the suited adsorbates, a correlation between kinetic coefficients vs. nitrogen contents is presented in Figure 4 for the more adsorptive mineral samples 264, 295, 303 and 308.

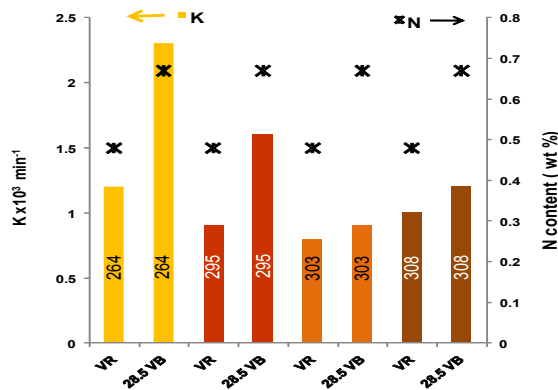


Figure 4. Kinetic coefficient at 120 min for VR and 28.5 VB vs. nitrogen content (wt %).

Results presented on Figure 4 clearly indicate that adsorbates nitrogen increases produced higher kinetic constants, particularly for samples 264 and 295. These findings suggest that minerals from these layers possess functional groups capable to interact with nitrogen compounds present in the studied adsorbates. This observation is in

line with a previous article that showed preferential retention of crude oils in cores as a function of their nitrogen contents⁸. In this sense, in order to get an insight of possible correlations among adsorption uptakes and minerals nature, infrared spectroscopy (DRIFT) was carried out for the 4 more adsorptive core samples devoid of their original bitumen components. As presented on Figure 5, differences in functional groups are detected within this set of samples.

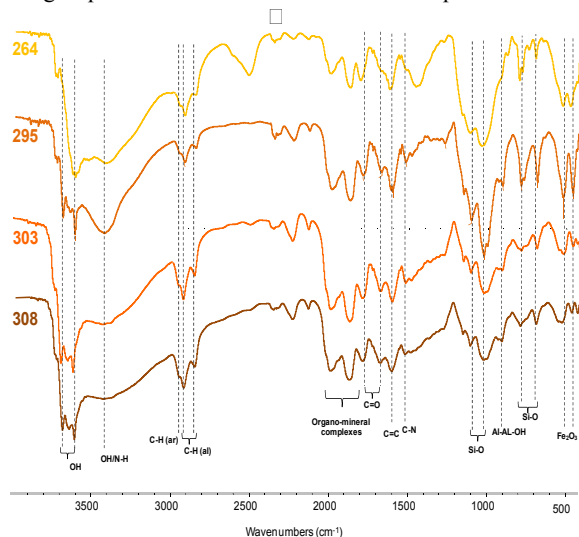


Figure 5. DRIFT analysis of the core samples before adsorption.

The FTIR spectrum shows that all the samples have similarities. Absorption bands appearing at 3000-2800, 1800, 1600, 1500-1350 cm^{-1} provide evidence that bitumen remains in all cases after Soxhlet extraction, maybe as occluded bitumen within inaccessible pore space and also as bonded bitumen participating in mineral-organic complexes. This behaviour indicates that stable complexes of bitumen functionalities are formed with the mineral matter and are thus resistant to solvent extraction⁹⁻¹¹. Bands corresponding to O-H within 3780 cm^{-1} to 3550 cm^{-1} plus the typical Si-O bands (1124 cm^{-1} and 1032 cm^{-1}) can be clearly observed and agree with recently published results for clays^{12,13}. Contribution of Fe_2O_3 for these solids is also deduced from the absorption bands observed at 538 cm^{-1} and 472 cm^{-1} .¹⁴ The fact that we have iron oxide present in such materials could also be a factor that contributes to the adsorption of those fractions. The presence of iron oxide plus clays in studied minerals is probably contributing to the adsorption of heavy fractions such as asphaltenes, in the same way as previously reported.¹⁴

Conclusions

The present study shows the adsorption behaviour of a VR from Athabasca crude and their corresponding thermal cracked product over mineral layers from a core reservoir sample. Sample heterogeneity produces a different uptake along the depth of a core. Thermal cracking of vacuum residual components leads to a product with greater affinity for the reservoir rocks, among the possible explanations of this affinity of the thermal cracked material for the samples employed could be the increase in aromaticity and in the content of nitrogen heteroatomic species. The type and content of minerals also influence adsorption. Preliminary evidence from surface characterization of the most adsorptive minerals reveals the presence of stable mineral-organic complexes after dichloromethane bitumen extraction. Presence of Fe_2O_3 and Si-O, Al-OH, -OH

functional groups like those present in clays suggest these sites are the most prone to interact with heavy hydrocarbon fractions such as the ones studied in this work.

Acknowledgments

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