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PRELIMINARY STUDIES ON ECONOMICAL REMOVAL OF NITROGENOUS COMPONENTS FROM HYDROCRACKED BITUMEN - PART I

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INTRODUCTION

This work has been done in accordance with the policy of Energy, Mines and Resources, Canada, of ensuring the effective use of Canada's mineral and energy resources.

One of the objectives of the Energy Research Program of CANMET (Canada Centre for Mineral and Energy Technology) is to develop economical processes to upgrade Canada's low-grade petroleum resources. A thermal-hydrocracking process has been developed at the Energy Research Laboratories for the upgrading of Athabasca bitumen using a once-through reactor (1,2,3).

The nitrogenous components in bitumens and heavy oils and their hydrocracking products are undesirable for various reasons. They, together with the associated polar compounds are responsible for the emulsion problems encountered in the hot water separation process of bitumen from sand. These components have also strong deleterious effect on the catalysts (4) in upgrading processes. The nitrogenous and polar components can cause the oils and bitumens to adhere strongly to the sand, clay or rock surfaces of the reservois, including the tar sands, which would adversely affect secondary and tertiary recovery of conventional oils. These recovery processes are becoming increasingly important in these times of depleting fossil fuel energy resources.

The separation, concentration and investigation of the nitrogenous components is considerably important for petroleum recovery and processing. Research on the separation of these components is not only an initial requirement for their chemical investigation but it could lead to an economically feasible process for their removal prior to refining. The separated nitrogenous components might prove to be valuable commodities e.g.; for use as additives to improve the performance characteristics of asphalts, building materials, as well as binders in briquitting and formed coking.

It has been demonstrated in our Laboratory (5) that a combination of highly cross-linked polystyrene based anion and cation exchange resins are capable of removing most of the nitrogenous components from bitumen and its products. These resins are expensive for use, and they would become degraded because of the precipitated heavy insoluble bitumen components. Therefore, there is a need to search for inexpensive and suitable materials to substitute these resins.

EXPERIMENTAL

Samples :

1. Hydrocracking Bitumen Product:

   A Great Canadian Oil Sands (GCOS) Athabasca Bitumen Sample was thermally hydrocracked in the CANMET hydrocracking process (3). The light ends and the heavy ends of the hydrocracking product distillate (Table 1) were combined proportionally (42.6 gm to 57.4 gm respectively) and used in this investigation. The combined product was deasphaltened using 5 volumes of n-pentane. The oil and resin part of the sample (maltenes) was treated by adsorbents for removing the nitrogenous components.

2. Adsorbents:

   Different adsorbents have been applied for removing the nitrogenous components from the hydrocracked Athabasca product (Table 2). When applicable, the adsorbents were ground and sieved to select the required particle size.

Experiments:

In all experiments 15g of the adsorbent materials were mixed with 30g of the hydrocracking product in 125ml conical flask, and shaken mechanically for designated periods. The adsorbent used, shaking periods and the conditions of adsorbent pretreatment are described in Table 3.

The following two series of experiments were carried out to investigate the efficiency of various coal materials and clays to remove nitrogen.

Series A

The hydrocracking product was treated as it is without prior deasphateneing. Also the adsorbents, were only air-dried but have not undergone any oxidation treatment.

Series B

The bitumen product was deasphaltened in this series. The adsorbents were oxidised by exposure to air at 150°C for 8 hours in a drying oven.

Nitrogen Determination:

The nitrogen content of the products was determined (parts per million) by microcoulometric titration method using Dohrmann MCTS-10 Nitrogen System.

The precision of the method in the range of 0.1 to 5000 ppm is between ± 0.05 and ± 3.20 ppm and relative precision is between ± 50.0% and ± 3.0% .

RESULTS AND DISCUSSION

In the oxidation of coal under moderate conditions, at temperatures below 200°C in air, the incorporation of oxygen into the coal structure would be expected to generate primarily carbonyl and carboxylic groups (6). This change in structure might enhance the adsorptive characteristics of the coal. The experimental results show that this is not true for removing nitrogenous components with the adsorbents and conditions used.

In Series A the nitrogen removed from the non-deasphatened hydrocracking product using air-dried adsorbents ranged from 5 to 13 % (Table 4).

The oxidised adsorbents at 150°C in a drying oven (Series B) were generally ineffective for any significant nitrogen removal (2 to 7 %, Table 4).

CONCLUSION

The used adsorbents, untreated or oxidised by air at 150°C, did not remove any significant amount of nitrogenous components from the hydrocracked Athabasca bitumen. Other adsorbents on more severe oxidation conditions should be sought for this purpose.

ACKNOWLEDGEMENTS

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TABLE 1

Characteristics of the Thermally-Hydrocracked Athabasca Products

(Run No. 78-T-23, 450°C, 1500 p.s.i., LHSV = 1.0)

Characteristic	Light End	Heavy End
Boiling Range, C°	up to 370°	Above 370°
Specific Gravity, $^{15}/15$ °C	0.831	1.005
Sulphur, wt % (x-ray)	1.58	3.14
Ash, wt %	---------	0.84
Conradson Carbon Residue, wt %	---------	12.3
Toluene Insolubles, wt %	---------	3.67
Pentane Insolubles, wt %	---------	13.90
Carbon, wt %	---------	84.52
Hydrogen, wt %	---------	9.93
Nitrogen, wt %	0.12	0.84

TABLE 2

Identification of Adsorbents Used in the Investigation

No.	Adsorbent
1	Lignite, Poplar River, Sask.
2	Sub-bituminous coal, Forestburg, Alta.
3	Low Volatile bituminous coal, Fording, B.C.
4	High volatile bituminous coal Devco 26, Sydney, N.S.
5	Medium volatile bituminous coal, Cardinal River, Alta.
6	Semi-anltracite, Canmore, Alta.
7	Sub-bituminous coal, Whitewood, Alta.
8	Peat, Springfield, MA.
9	Sandy Stoneware clay, Eastend, Sask.
10	Saskatchewan ball clay, Flintoft, Sask.
11	'Blue' champlain sea clay, Billings Bridge, Ottawa
12	Lignite ash, furnace bottom, the ERL Combustion process

TABLE 3

Experimental Conditions of Nitrogen Removal from Hydrocracked Athabasca Bitumen Using Adsorbents

	Series A	Series B
Adsorbent No. (See Table 2)	1-12	1,8,12
Hydrocracked product	non-deasphaltened	non-deasphaltened
Oxidation of adsorbent, hrs.	untreated	8 hrs. in oven *
Adsorbent / Oil (wt/wt)	½	½
Adsorbent particle size, mesh.	-35 X 0	-35 X 0
Shaking time, hr.	1	1

* This oxidation was performed in a drying oven at 150°C, with occasional stirring.

TABLE 4

Removal of Nitrogenous Components from Athabasca Bitumen Hydrocracking Product

- Nitrogen content of hydrocracking product (non-deasphaltened) used in Series A = 4130 ppm
- Nitrogen content of hydrocracking product (deasphaltened) used in Series B = 810 ppm

	Adsorbent No.	Nitrogen Content (ppm)	% Nitrogen Removal
Series A	1	3586	13.2
	2	3804	7.9
	3	3696	10.5
	4	3913	5.3
	5	3913	5.3
	6	3913	5.3
	7	3913	5.3
	8	3804	7.9
	9	3804	7.9
	10	3804	7.9
	11	3804	7.9
	12	3913	5.3
Series B	1	751	7.3
	8	796	1.7
	4	756	6.7