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Majid, Abdul; Clancy, Vince; Sparks, B. D.

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dine, the activity for C-N hydrogenolysis diminished with a decrease in the number of denitrogenation sites, even though the intermediate hydrogenation of acridine was enhanced by sulfiding.

Conclusions

(1) Sulfiding of the reduced catalyst enhanced the activity for the C-N hydrogenolysis at all reaction temperatures during carbazole hydrodenitrogenation.

(2) The addition of the sulfur compounds depressed the C-N hydrogenolysis, which became the rate-determining step when the intermediate hydrogenation attained equilibrium at 360 °C.

(3) The presence of a small amount of CS₂ in the solution promoted the catalytic activity of the reduced catalyst for the C-N hydrogenolysis at 360 °C since CS₂ was converted to hydrogen sulfide, which sulfided the catalyst surface during the reaction.

(4) When the intermediate hydrogenation of carbazole was not in full equilibrium with the reduced and sulfided catalyst at 300 °C, the sulfur compounds depressed the hydrogenation of carbazole, which led to decreased C-N hydrogenolysis.

Registry No. Mo, 7439-98-7; carbazole, 86-74-8; bicyclohexyl, 92-51-3; α -ethylbicyclo[4.4.0]decane, 1008-17-9; hexylcyclohexane, 4292-75-5.

Coagglomeration of Athabasca Petroleum Cokes with Sulfur Sorbents as a Means of Reducing Sulfur Emissions during Combustion[†]

Abdul Majid,* V. P. Clancy, and Bryan D. Sparks

*Division of Chemistry, National Research Council of Canada,
Ottawa, Ontario K1A 0R9, Canada*

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The low volatiles and high sulfur content of the coke produced during the upgrading of Athabasca bitumen makes it unsuitable as a fuel. However, the coke can be used as an adsorbent to recover heavy oil or bitumen from process waste streams by using a liquid-phase agglomeration technique. It has been found that bitumen can act as a collector for certain sulfur dioxide capture agents, allowing them to be incorporated into the coke agglomerates during the oil recovery operation. Three sulfur sorbents—lime, hydrated lime, and limestone—and cokes from both Suncor delayed coking and Syncrude fluid coking operations were used in this investigation. This coagglomerated material could be used as an ancillary fuel for generation of process energy for bitumen recovery. During combustion of the coagglomerates, sulfur dioxide capture was found to depend mainly on the calcium to sulfur mole ratio, the combustion temperature, and the type of coke. The efficiencies of the three agents used in this investigation for reducing sulfur dioxide emissions have been compared.

In previous work the authors have used petroleum coke to recover bitumen or heavy oil from waste water produced in oil sands surface mining or in situ recovery operations by means of the spherical or liquid-phase agglomeration technique.¹⁻⁴ In this process the addition of finely divided hydrophobic collector particles to the agitated waste water results in adsorption of the residual organic liquids by the hydrophobic solids and then the formation of agglomerates of the coke particles due to cohesion between the adsorbed liquid films. The end result of the waste-water treatment process is a cleaned water stream and a particulate solid containing the coke and oil. The latter material has improved combustion properties relative to those of the original low-volatile coke. However, the high sulfur content of this material makes it unsuitable for use as an ancillary fuel for process energy production.

The objective of this investigation was to develop an economically attractive method by which the agglomerates produced during waste water treatment could be utilized

directly as a boiler fuel without serious environmental damage. The combustion of these agglomerates with limestone addition, such as in a fluidized-bed reactor, could be one way to achieve the required reduction in sulfur dioxide emissions.^{5,6} However, it has been demonstrated^{1,5} that this approach requires relatively high calcium to sulfur mole ratios, even with ash recycle, to produce acceptable reductions in sulfur dioxide emissions. The development of combined fuel-sorbent pellets or briquettes for use as a sulfur dioxide control method has been reported^{7,8} to give superior sulfur dioxide emission control during combustion.

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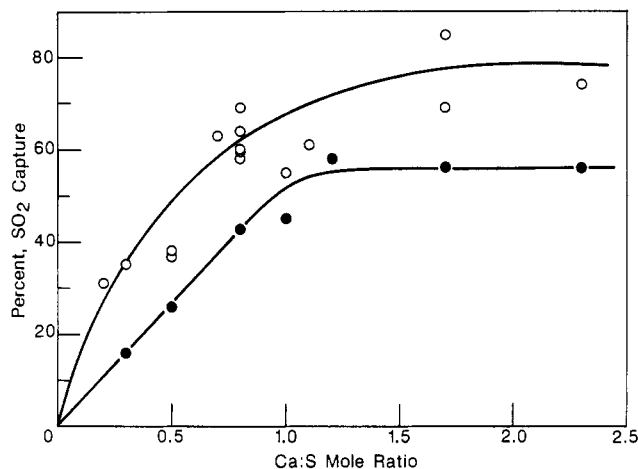


Figure 1. Effect of temperature and calcium to sulfur ratio on SO_2 capture by limestone. Ashing temperatures: (●) 460 °C; (○) 1000 °C.

Application of this process to the system under investigation here would require an additional pelletizing operation after the initial oil recovery step. However, if the surface of the hydrophilic sulfur sorbent could be conditioned to render it hydrophobic, then a wet agglomeration process^{9,10} could be used to produce a coagglomerate of coke and sorbent during the waste-treatment process itself. Fortunately, Athabasca oil sands bitumen, the residual oil in these waste streams, is a good wetting agent for both the hydrophobic coke and the hydrophilic sorbent. The present research was designed to study the feasibility of introducing sulfur capture agents into the agglomerates as they were being formed during the waste-water-treatment process.

Experimental Section

Procedure. Coke was mixed with a known amount of a sulfur-sorbent material and then dispersed in water by means of a Waring Blender. An appropriate amount of a surface conditioning agent was then added, if needed, and the contents were agitated at 250 revolutions/s (rps) for 15 s. At this stage the blending speed was lowered to 120 rps. Bitumen was added slowly, while blending, until a discrete agglomerate phase was obtained; the agglomerates were then separated from the aqueous phase by screening. A portion of the agglomerates was used for analysis of bitumen, coke, and ash content by using a procedure described elsewhere.² The second portion of the agglomerates was dried at 100 °C to constant weight.

Agglomerates Combustion. The dry agglomerates were weighed in a tared porcelain crucible, and the crucible was placed into a muffle furnace preset at the desired temperature. After completion of combustion the crucible was removed from the furnace and allowed to cool in a desiccator before analysis.

Sulfur Analysis. The sulfur content of the various samples was determined by X-ray fluorescence spectrometry. The sulfur fixed in the ash during combustion was expressed as a percentage of the total sulfur in the original sample.

Results and Discussion

It was determined that cokes from both Syncrude fluid coking and Suncor delayed coking operations could be successfully coagglomerated from aqueous slurries with varying amounts of lime, hydrated lime, or limestone by using bitumen as the binder. Addition of a small quantity of conditioning agent such as sodium hydroxide, oleic acid, or a petroleum sulfonate (WITCO TRS 10/80) improved

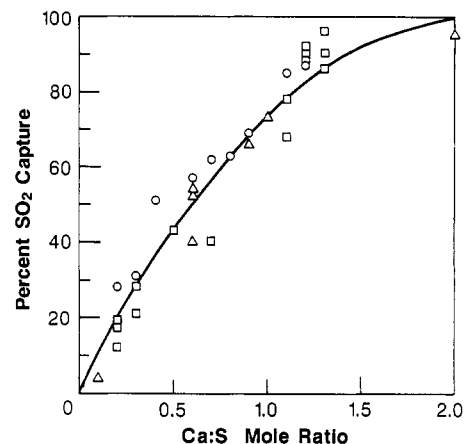


Figure 2. Comparative SO_2 capture efficiencies of various sorbents for Suncor coke: (○) limestone; (△) lime; (□) hydrated lime.

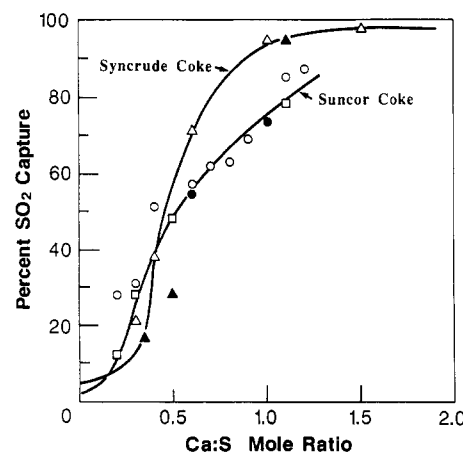


Figure 3. Comparative reductions in the sulfur dioxide emissions from the combustion of two coke-sorbent agglomerates: (△) Syncrude-limestone; (○) Suncor-limestone; (▲) Syncrude-lime; (●) Suncor-lime; (□) Suncor-hydrated lime.

the coagglomeration of the components.

On combustion, a portion of the sulfur dioxide was captured by the sorbent. As expected,¹ the efficiency of sulfur dioxide capture was a function of the calcium to sulfur mole ratio in the agglomerates and the combustion temperature, as shown in Figure 1.

A comparison of the three sorbents tested (lime, hydrated lime, and limestone) is illustrated on the plots shown in Figure 2. These experiments were carried out at a combustion temperature of 1000 °C. In this series of tests each batch of agglomerates was prepared in the presence of sodium hydroxide, which has been shown to result in activation of sorbents.¹¹ With the observed scatter of results, no significant difference in sulfur capture between the three sorbents could be detected. Also, comparison of the combustion data for agglomerates containing limestone, with and without an activator, showed little difference in sulfur capture efficiency at 1000 °C.

The fact that the limestone used in this series of tests gave results as good or better than lime or hydrated lime has considerable economic significance. The cost ratio of lime to limestone on a molar basis may vary from 2 to 4, depending on the transportation distance.¹² Even the costs for transportation and handling of limestone tend

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to be lower than for lime because limestone can be transported in open trucks. Also, limestone is readily available in the Athabasca region of Alberta.

In Figure 3 a comparison of the efficiency of the desulfurization process has been made for the two cokes investigated. These results were obtained under identical experimental conditions at a combustion temperature of 1000 °C. From the plots, sulfur capture is more efficient for Syncrude coke than for Suncor coke at higher calcium to sulfur ratios. Thus, at a calcium to sulfur mole ratio of about 1:1, 94% sulfur retention was observed for Syncrude coke compared with a value of 80% for Suncor coke. The reason for this difference is not understood.

According to the findings of Schneider and George¹³ the presence of calcium has a beneficial effect on the acid leaching of nickel and vanadium from coke ash. Hence, coagglomeration of coke with calcium compounds also will have the added advantage that the ash from the burnt

agglomerates will be more suitable for heavy-metal recovery as a byproduct of the combustion process.

In conclusion, it can be stated that waste coke produced in the upgrading of Athabasca bitumen can be successfully coagglomerated with sulfur dioxide capture agents during the recovery of bitumen or heavy oil from aqueous waste streams produced during oil sands processing. The resulting agglomerates have improved combustion properties and lower sulfur emissions compared with those for the original coke. The decrease in sulfur dioxide emitted on combustion was found to depend on the calcium to sulfur mole ratio, combustion temperature, and the type of coke. Better results were obtained for Syncrude fluid coke than for Suncor delayed coke.

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Registry No. SO₂, 7446-09-5; Ca(OH)₂, 1305-62-0.

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Surface Tension of Bitumen from Contact Angle Measurements on Films of Bitumen

E. I. Vargha-Butler,[†] T. K. Zubovits, C. J. Budziak, and A. W. Neumann*

Department of Mechanical Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

Z. M. Potoczny

Coal Research Laboratory, CANMET, EMR, Devon, Alberta T6G 2C2, Canada

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Advancing contact angles, θ_A , of water and glycerol were measured on films of bitumen. The bitumen was obtained by extracting different raw oil sands with various organic solvents. The films were prepared by film casting the bitumen from solutions (using the same solvent that was used for the extraction). The contact angles of both liquids were determined on bitumen surfaces by means of the sessile drop method at room temperature. The surface tensions, γ_{SV} , of the quasi-solid bitumen films were calculated from the contact angles by means of an equation of state approach. It was found that contact angles measured with water and glycerol depended on the solvent used for the bitumen extraction. The surface tension, γ_{SV} , of the quasi-solid bitumen films calculated from the contact angles agree with the surface tensions determined at elevated temperatures by means of the Wilhelmy plate technique. Thus, the contact angle method provides an independent technique for the surface characterization of bitumen at ambient temperatures.

Introduction

In preceding papers^{1,2} we reported the surface tension of bitumen determined by direct measurements using a modified Wilhelmy plate technique.³ The surface tension of bitumen was measured by temperature scanning from 40 to 90 °C, since at lower temperatures the high viscosity of bitumen does not allow conventional surface tension determination. The bitumen samples were obtained from various raw oil sands by extraction with several solvents

of different polarity and by centrifugal separation, i.e., without solvents. It was found that the surface tension of bitumen extracted with organic solvents depends on the solvent used for the extraction and that it is lower than that obtained by centrifugal separation. The differences

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[†] Present address: College of Pharmacy, Dalhousie University, Halifax, Nova Scotia B3H 3J5, Canada.