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CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

CHEMICAL CHARACTERIZATION OF FEEDSTOCK
AND HYDROCRACKED PRODUCTS

by

Albert E. George

(Presented at the meeting with the Venezuelan Delegation
to discuss the CANMET Hydrocracking Process,
December 4, 1979).

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CHEMICAL CHARACTERIZATION OF FEEDSTOCK
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INTRODUCTION

Working on bitumens and heavy oils poses certain problems in the areas of recovery, processing and analysis. All these problems are attributed to the chemical nature of these materials. They are asphaltic, and contain high amounts of sulphur, nitrogen and metals. The aromatic content is considerably high, and most of it is in the form of polycyclic aromatics.

Emulsion formation in the hot water extraction process of bitumens and in in-situ recovery is related to the presence of high amounts of nitrogenous and polar material in the bitumens. These components also cause the oils to adhere to the reservoir rocks in secondary and tertiary recovery processes.

Polynuclear aromatics have a definite role in coke formation during processing. This causes reactor fouling and catalyst deactivation. The nitrogenous compounds, particularly the basic types, are known for their deleterious effect on catalysts.

In all these problems the conventional routine analyses by physiochemical methods are not adequate. Study of the chemical configurations of the different hydrocarbons, sulphur and nitrogenous compounds is necessary. Most of the methods for chemical characterization of conventional oils and their products have to be modified or new method developed to be used in bitumen and synfuels. The latter are more complex in composition and less stable thermally. The modifications aim at improving analysis and speeding up the methods.

I will present examples of projects in which we modified characterization methods and used them for Canadian bitumen and heavy oils as well as their products from the CANMET hydrocracking process.

RAPID CHROMATOGRAPHIC PROCEDURE FOR CHEMICAL CHARACTERIZATION OF SYNTHETIC FUEL NAPHTHA

Significance

1. Potential for BTX production.
2. Choosing reforming strategy to upgrade the octane number without using lead additives.

Accomplishment

In 90 minutes per sample of 30 ul obtain the following information:

1. Complete true boiling point data.
2. Hydrocarbon-type distribution (saturates, olefins and aromatics).
3. Sulphur content.
4. GC/MS analysis of all major components of the C₅-C₁₃ range.

Slides

1 and 2.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOR ANALYSIS OF POLYNUCLEAR AROMATICS

A superior HPLC system is developed for analysis of PNA. The Silica-R(NH₂)₂ sorbent with n-heptane and n-heptane/CH₂CL₂ mobile phase shows selectivity centered on ring type up to 4 rings.

Slide 3

MODIFICATION OF THE USBM-API PROCEDURE FOR HYDROCARBON TYPE ANALYSIS OF HEAVY PETROLEUM DISTILLATES

Accomplishment

1. Time of analysis/sample considerably reduced.
2. Sample size, gel and solvents volume scaled down by a factor of 10.
3. The polyaromatic-polar fraction resolved to three fractions of different composition.

Slide 4

EFFECT OF THERMAL HYDROCRACKING ON HYDROCARBON-TYPE DISTRIBUTION IN
ATHABASCA BITUMEN

Hydrocarbon-type conversions discussed.

Slides 5,6

Further Work

- Lloydminster hydrocracked products have been investigated.
- Investigation of Cold Lake hydrocracking products is underway.

MODIFICATION OF ION-EXCHANGE CHROMATOGRAPHIC METHOD FOR NITROGEN-TYPE
ANALYSIS IN SYNTHETIC FUELS

Accomplishment

1. Time of analysis per sample considerably reduced.
2. Pretreatment step with FeCl_3 *precluded*
3. Polar material quantitatively separated into six fractions with minimum amounts of solvent.

Slides 7,8,9.

EFFECT OF HYDROCRACKING ON THE DISTRIBUTION OF NITROGENOUS COMPONENTS IN
ATHABASCA BITUMEN

1. Fractions have higher nitrogen content due to migration of these components from asphaltenes and residual fractions.
2. Separation of nitrogenous compounds from non-polar material improves.
3. Acids eliminated (decarboxylation).
4. Basicity increases with severity of hydrocracking.
5. Carbozoles, indoles and pyrroles increase considerably.

Slides 10,11,12

EFFECT OF HYDROCRACKING ON SULPHUR COMPOUND-TYPE DISTRIBUTION IN NAPHTHA
OF ATHABASCA BITUMEN

1. Overall sulphur amount decreases.
2. Main sulphur-types in hydrocracking naphtha are residual sulphur (thiophenic), aliphatic sulphides and aromatic sulphides in descending order.

3. The catalytic product has higher mercaptans and aromatic sulphides, and lower residual and aliphatic sulphides than the non-catalytically hydrocracked product.

FURTHER WORK

Hydrocracking naphtha products of Lloydminster oil have been investigated. Work on Cold Lake products is underway.

Slides 13,14,15.

CANMET HYDROCRACKING PROCESS
Meeting with a Venezuelan Delegation
December 4, 1979

AGENDA

09:30-
11:30 hrs

Morning Session - Plant Tour

1. Introductory Comments by J.M. Denis, Manager of the Synthetic Fuels Research Laboratory.
2. Tour of the SFRL facilities:
 - (a) Building No. 4 - hydrocracking pilot plants
 - (b) Building No. 5 - catalyst development
 - (c) Building No. 6 - coal liquefaction - distillation

11:30-
13:00 hrs

Lunch

13:00-
16:30 hrs

Afternoon Session - Technical Presentations

Theme: Improvements to the CANMET Hydrocracking Process

Session Chairman: J.M. Denis

1. "Role of the Additive as a Coke Suppressing Agent" by Dr. K. Belinko - Bitumen Processing Section.
2. "Role of the Additive as a Demetalization Agent" by Dr. D. Patmore - Bitumen Processing Section.
3. "Processing Strategies" by Dr. R. Ranganathan - Bitumen Processing Section.
4. "Prediction of Operability from Bench Scale Studies" by Dr. J. Kriz - Catalysis Development Section.
5. "CANMET Pitch - A Valuable Component in Metallurgical Coke" by Dr. K. Belinko - Bitumen Processing Section.
6. "Pitch Conversion by Catalytic Pyrolysis and Gasification" by Dr. M. Ternan - Catalysis Development Section.
7. "Chemical Characterization of Feedstock and Hydrocracked Products" by Dr. A. George - Research on Bituminous Substances Section.

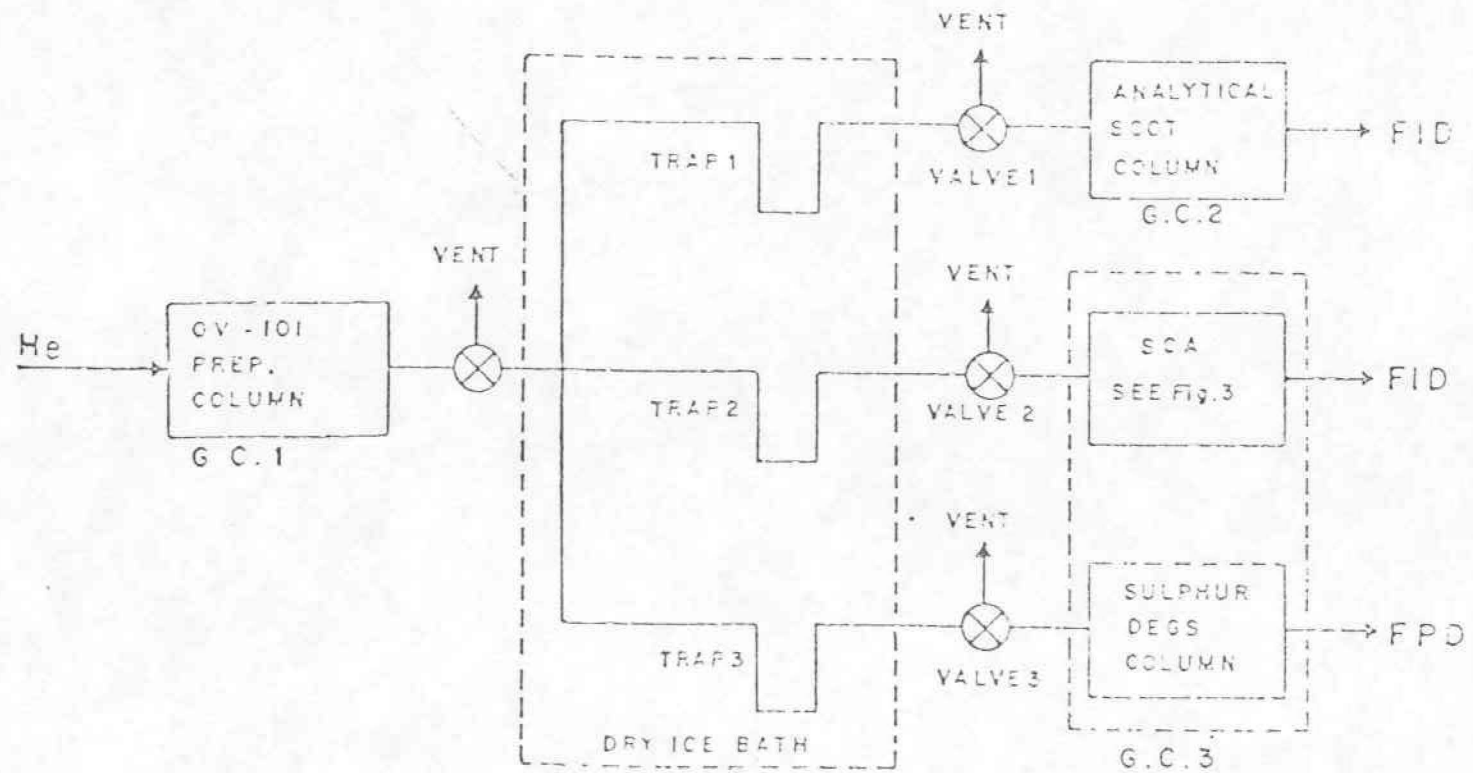
Attendees

1. Venezuela: Franzao Marruffo Intevep
 Edgard Coronado Corpoven
 Domingo Marsicobetre Corpoven (sends regrets)
 Luis Soler Corpoven (sends regrets)

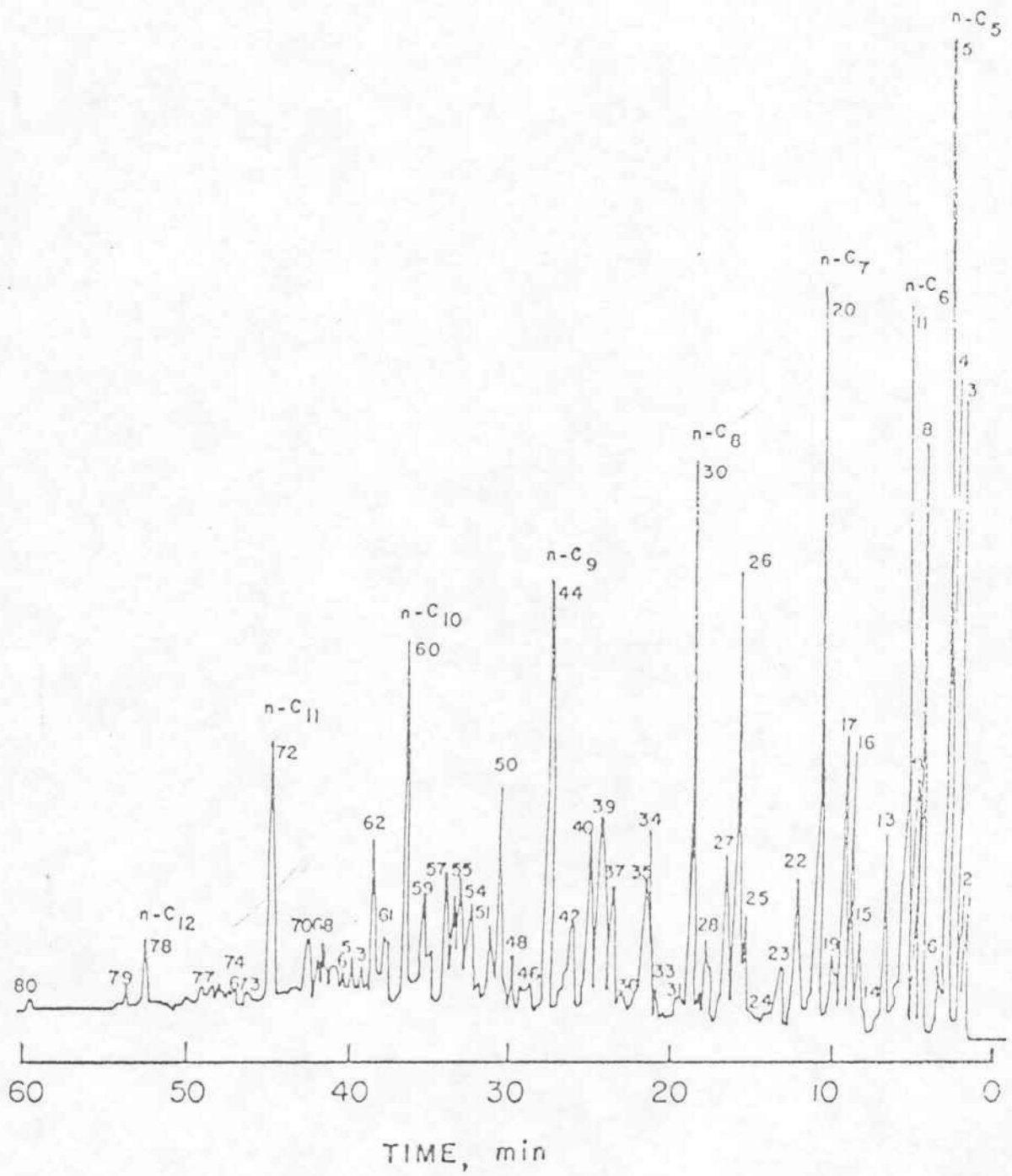
2. Petro-Canada: George Lunin
 Dr. Michael Menzies
 E.K. Perkins

3. CANMET: Dr. D.A. Reeve Director, Energy Program Office
 Dr. Henry Sawatzky Asst. Dir., Energy Program Office
 J.M. Denis Manager, Synthetic Fuels
 Research Laboratory

 Dr. R. Kanganathan
 Dr. D. Patmore
 Dr. K. Belinko
 Dr. M. Ternan
 Dr. J. Kriz
 ✓ Dr. A. Gebрге



SLIDE 1 CHROMATOGRAPHIC SYSTEM FOR NATURAL GAS ANALYSIS



SLIDE 2 CHROMATOGRAM OF NAPHTHA FRACTION OF HYDROCRACKED ATHABASCA BITUMEN

SLIDE 3
HPLC FOR PAH ANALYSIS

SIGNIFICANCE

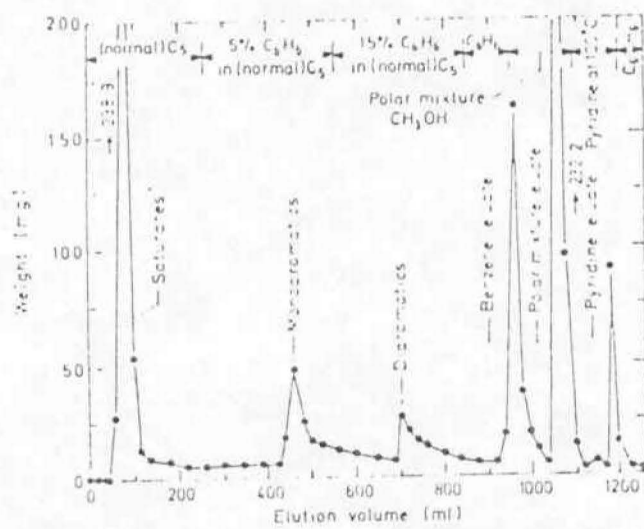
- POSSIBLE ROLE IN COKE FORMATION
- CATALYST DEACTIVATION
- FOULING UP REACTORS
- POTENTIAL CARCINOGENS

SELECTIVITY

- 46 PAH ON 7 HPLC SILICA-BASED POLAR BONDED PHASE SORBENTS IN NORMAL MOBILE PHASE
- REVERSE PHASE SILICA-C₁₈ BASED SYSTEM
- SILICA-R(NH₂)₂ SORBENT SUPERIOR, SELECTIVITY CENTERED ON RING TYPE UP TO 4 RINGS.
PHENYL SUBSTITUTION DOES NOT INCREASE THE PARENT AROMATIC RETENTION.

RESULT

- FRACTIONS OF AROMATICS ARE SEPARATED FROM FEEDSTOCKS AND PROCESSING PRODUCTS ON BASIS OF NUMBER OF RINGS.
- FURTHER ANALYSIS BY GC-MS IN A MORE CHEMICALLY EFFICIENT MANNER.

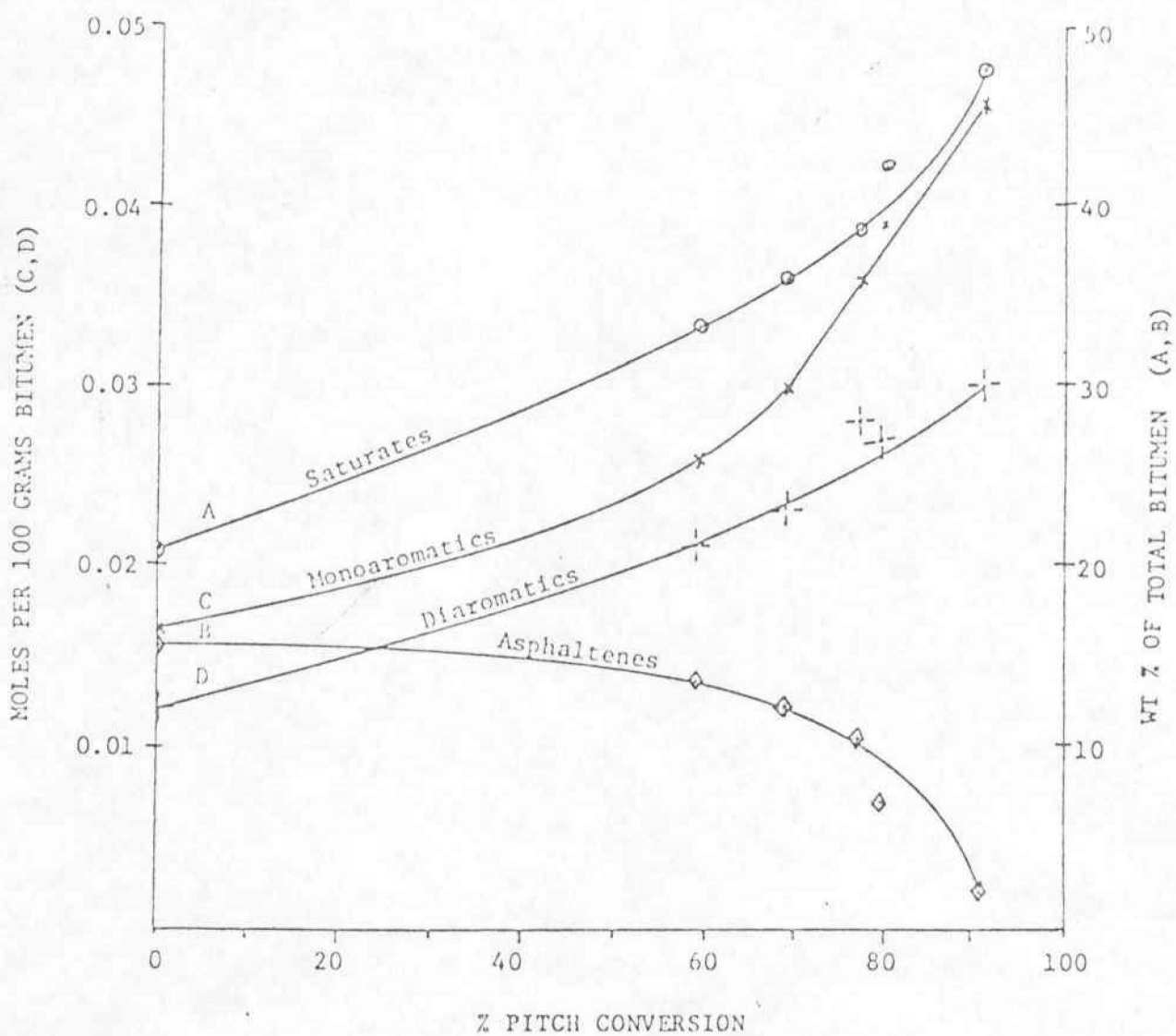


Slide 4 Liquid-solid chromatographic separation of deasphalted Athabasca bitumen

SLIDE 5
COMPOUND TYPE DISTRIBUTION (% BY WT)

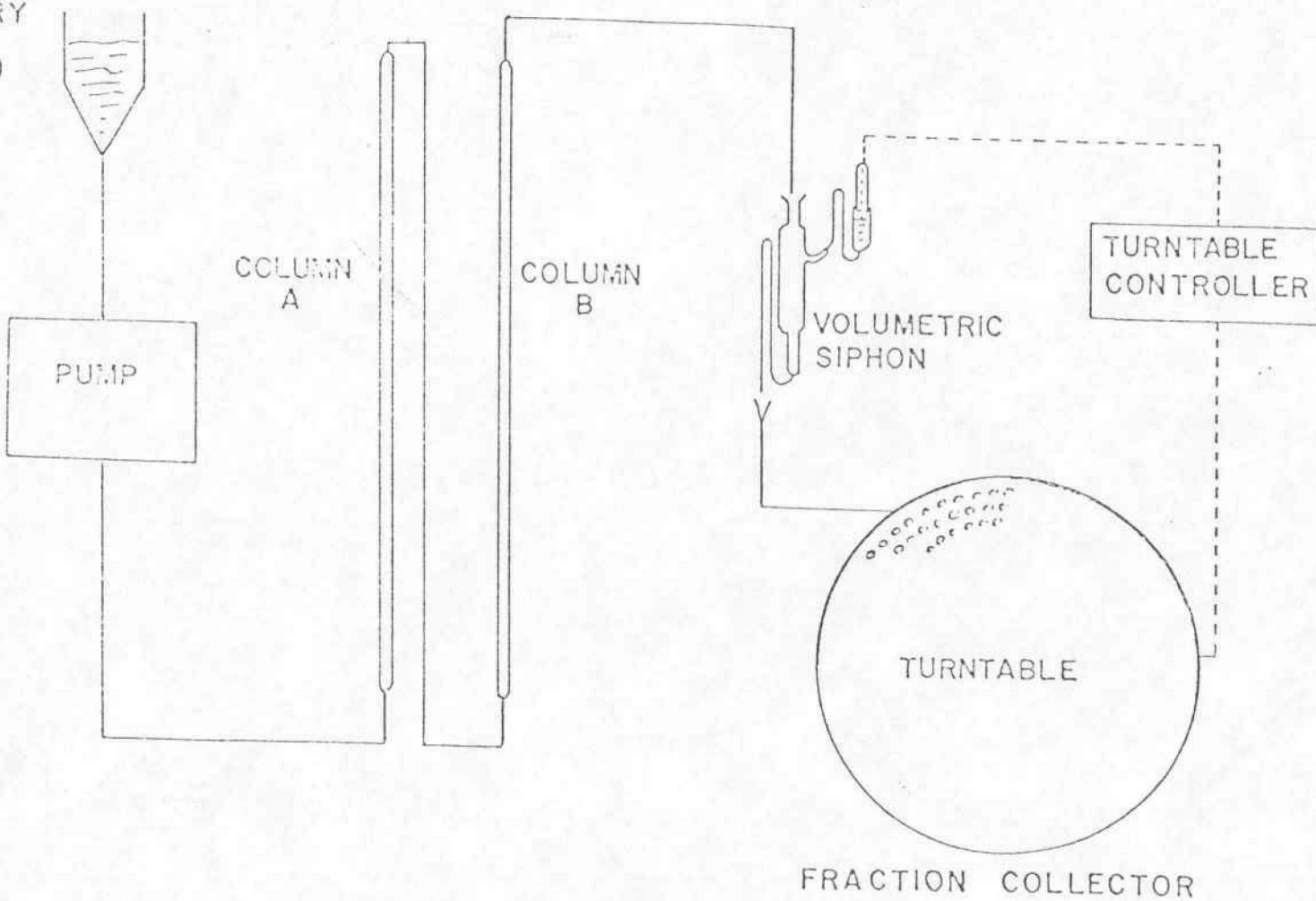
		<u>SATURATES</u>	<u>MONONUCLEAR AROMATICS</u>	<u>DINUCLEAR AROMATICS</u>	<u>POLYNUCLEAR AROMATICS</u>	<u>POLAR COMPOUNDS</u>	<u>BASIC COMPOUNDS</u>	<u>ASPHALTENES</u>
FFFD		21.0	7.8	11.0	20.1	19.0	5.7	15.3
LHSV-2,	435°C	33.4	9.3	10.5	14.2	12.3	2.3	13.4
LHSV-2,	445°C	36.1	10.1	10.7	12.9	11.6	2.1	12.3
LHSV-2,	455°C	38.9	10.5	11.0	11.7	9.3	1.6	13.5
LHSV-1,	445°C	42.5	10.5	10.1	11.1	10.3	1.2	7.0
LHSV-1,	460°C	47.8	11.5	9.7	9.1	8.3	0.9	1.7

SLIDE 6

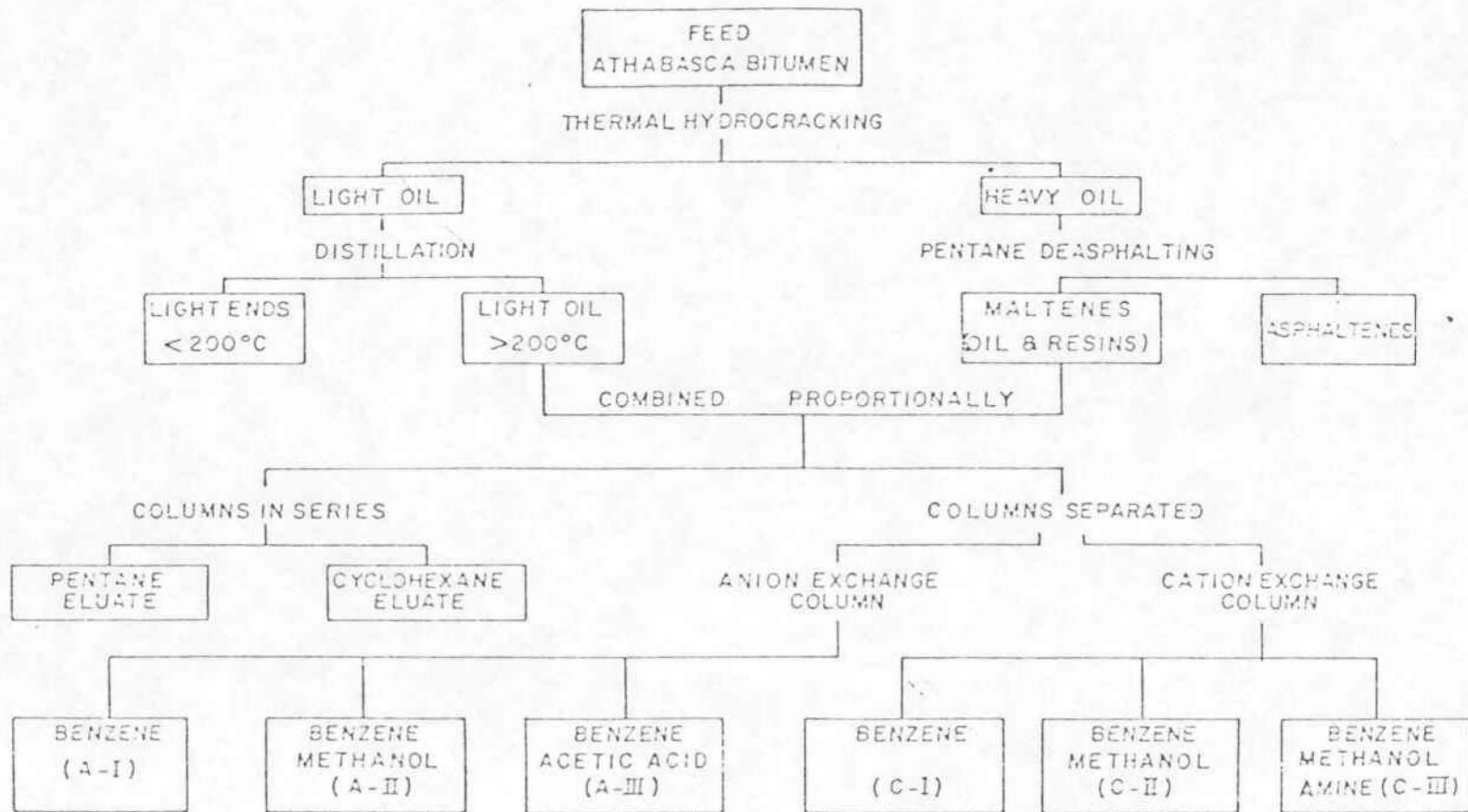


The Effect of Hydrocracking on Saturate, Monoaromatic and Asphaltene Contents in Athabasca Bitumen

SEPARATORY
FUNNEL (S)



SLIDE 7 Ion-Exchange Chromatography System



HYDROCRACKING AND SEPARATION (SCHEMATIC)

SLIDE 9

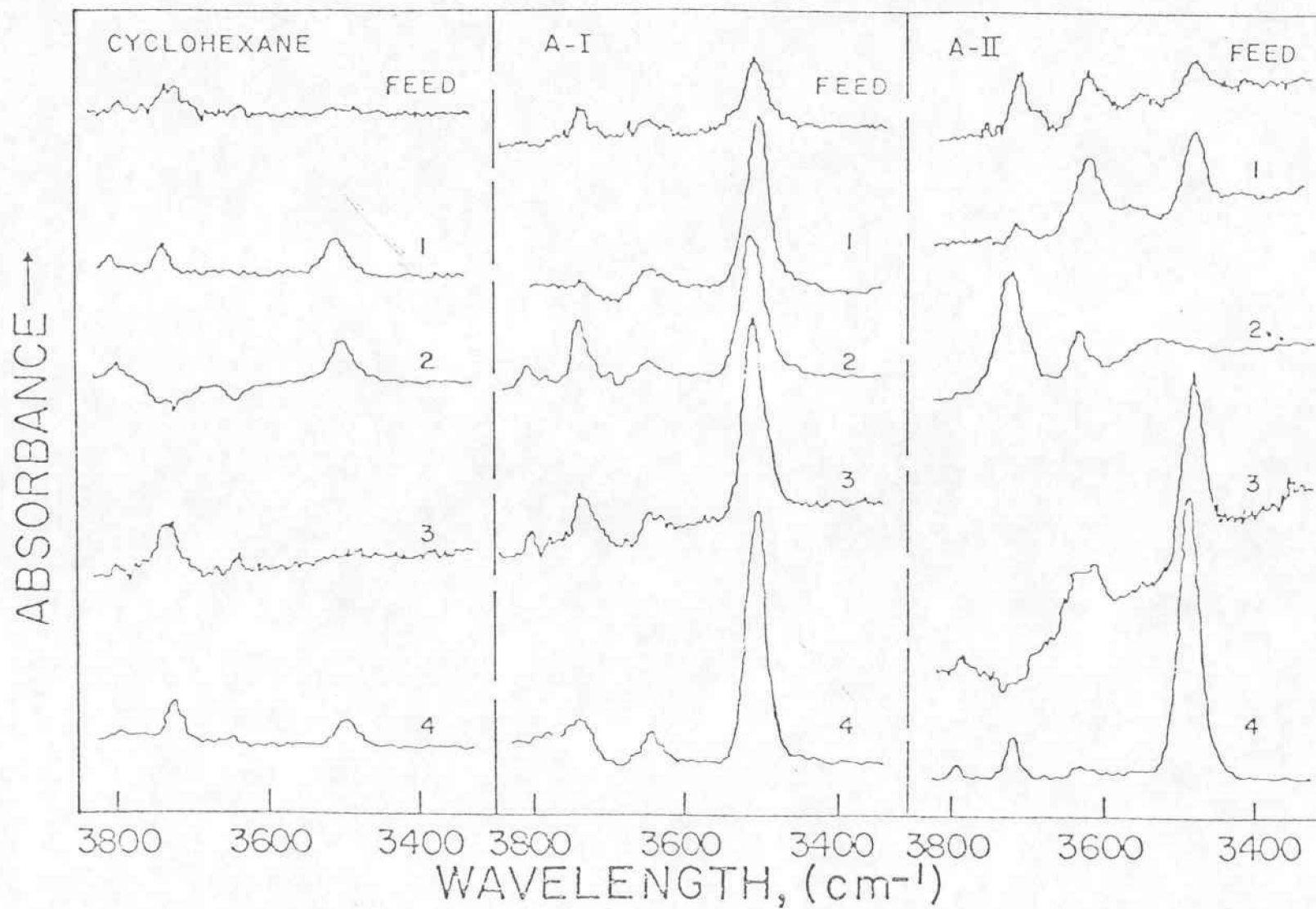
Ion Exchange Chromatography of Alberta Basin Bitumen and Oils

	Wt % of Total Sample			
	Athabasca	Cold Lake	Lloydminster	Medicine River
Cyclohexane Eluate	4.32	2.16	2.62	0.37
Eluate from Anion Exchange Resin				
Benzene	6.23	5.44	6.16	1.34
Benzene-Methanol	1.92	0.92	1.00	0.16
Benzene-Methanol-CO ₂	2.15	0.61	0.30	0.50
Benzene-Acetic Acid	0.65	0.24	0.32	0.40
Eluate from Cation Exchange Resin				
Benzene	3.62	3.04	2.68	0.66
Benzene-Methanol	1.49	1.35	0.62	0.24
Benzene-Methanol-Isopropyl Amine	1.29	1.02	0.58	0.10

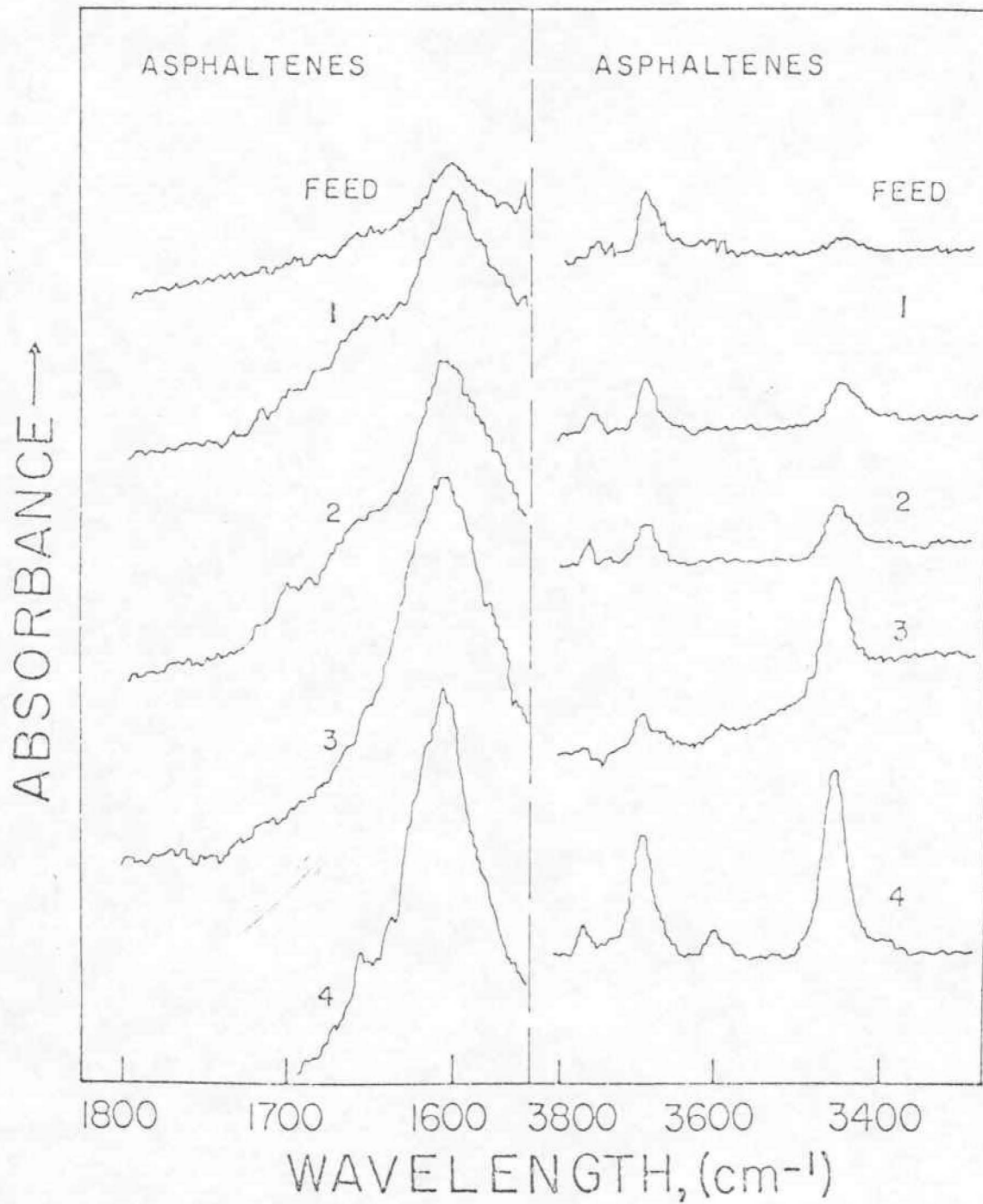
SLIDE 10

Milliequivalents of Pyrrolic Compounds
in 100 grams of the Bitumen and Hydrocracked Products

<u>Sample</u>	<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch Conversion	wt %	26	49	79	89
Pentane Eluate	-	-	-	-	-
Cyclohexane Eluate	-	0.34	0.17	-	0.51
Anion Eluate, A1	1.01	2.01	3.24	2.12	1.84
A11	0.34	0.56	0.70	1.01	3.35
Cation Eluate, C1	0.23	0.51	0.70	0.24	0.62
C11	-	-	-	0.13	0.20
Asphaltenes	1.72	1.87	1.02	1.47	2.32



SLIDE 11 - INFRARED SPECTRA OF AIIII ELUATES



SLIDE 12 INFRARED SPECTRA OF ASPHALTENES

SLIDE 13

Gross Composition of Hydrocracked Products

Sample No.	Operating Temp. °C	Hydrogen Chemical Consump. m ³ API/t	Pitch Conversion wt %	wt % of total bitumen product		
				Naphtha up to 200°C	Oil & Resins above 200°C	Asphaltenes
1	410	28.2	26.1	3.9	82.2	10.8
2	420	37.9	36.8	7.8	80.4	10.4
3	430	54.0	49.3	10.6	76.3	9.8
4	470	212.7	89.1	17.4	68.8	4.3
5C*	460	179.3	83.5	11.5	76.5	3.9

* Catalytic hydrocracking product (cobalt-molybdena oxides on coal base)

sSLIDE 14

Sulphur-Type Distribution in Naphtha Product
(wt % of sulphur in sample)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Mercaptans	0.052	0.067	0.056	0.010	0.037
Aliphatic sulphides	0.64	0.52	0.43	0.21	0.07
Aromatic sulphides	0.28	0.28	0.26	0.14	0.09
Residual sulphur	0.83	0.92	0.82	0.51	0.12
Total sulphur	1.80	1.79	1.57	0.87	0.32

SLIDE 15

Sulphur-Type Distribution in Naphtha Product
(sulphur-type as percentage of total sulphur)

<u>Sample</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5C</u>
Mercaptans	2.9	3.8	3.6	1.2	11.7
Aliphatic sulphides	35.5	29.1	27.4	24.1	22.1
Aromatic sulphides	15.5	15.7	16.6	16.1	28.4
Residual sulphur	46.1	51.4	52.4	58.6	37.8