

METHANE ASSISTED CATALYTIC CONVERSION OF HEAVY CRUDES

- Highly feed and product flexible
- Dramatic cost saving
- Significant CO₂ emission reduction

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TECHNOLOGY HIGHLIGHTS



- A wide variety of petroleum-based feeds ranging from the lightest like naphtha to the heaviest such as asphaltene can be readily upgraded to high value-added fuel or chemicals through a novel catalytic process under methane rich environment with a simple but robust fixed bed configuration.
- Depending on the charged low-cost catalyst, the highly customized product stream can be formed, which can be simply further refined for end use.

GROUP INTRODUCTION

- Green Catalysis Research Group (GCRG) is established in Calgary, Canada in July 2012. GCRG has successfully educated more than 80 highly qualified personnel and disseminated more than 70 peer-reviewed journal articles, 30 patents and 5 book and book chapters. GCRG has grown its research interests in heterogeneous catalysis and its applications in clean energy conversion and environmental control including the following ongoing projects:
 - Heavy oil upgrading using natural gas
 - Light olefin upgrading using natural gas
 - Low-cost carbon source pyrolysis under natural gas
 - Municipal solid wastes utilization
 - Low temperature NO_X control
 - Natural gas storage for vehicular application
 - H₂ production from low-cost carbon sources



RESEARCH CAPACITY

 Our research facilities are well accommodated in a lab space of ~120 m² fully equipped with state-of-the-art infrastructure and instruments (~ \$ 6.5 million CAD).









RESEARCH FACILITIES - REACTOR SYSTEMS



Two continuous reactor systems with pressure rating from 0.1 to 10 MPa, temperature range of 25 ~ 1200 °C, and gas velocity of 0 ~ 1,000,000 hr⁻¹, liquid flow rate up to 10 mL/min.

Five batch high temperature, high pressure batch reactor systems with capacity of 100, 300, and 500 mL.







RESEARCH FACILITIES – CATALYST SYNTHESIS EQUIPMENT















GC-MS



FTIR with in-situ chamber and gas cell





Micro-GC

Gas pycnometer



ICP-OES



Density Meter





Extraction-Distillation Apparatus



Computational Workstation

Micro-GC for field operation







Vapor pressure osmometer



TAN/Br No. titrator



KF titrator



Simulated distillation analyzer



TGA-DSC



Viscometer



Surface Area and Porosimeter System



UV-Vis Spectrometer



Online Mass Spectrometer



Chemisorption System (AutoChem II 2920)



Benchtop XRD (Bruker D2 PHASER)

BACKGROUND INTRODUCTION

Heavy crude

- Iong carbon chain (> 30) with complicated molecular structure (e.g. polyaromatics)
- \square high viscosity (1×10³-2×10⁶ cP)
- High impurity content (e.g., Heavy metals, S, N)
- □ low H/C molar ratio





UNSATURATION FORMATION

Heavy oil cracking

- Reduce carbon chain length
- Break polyaromatic structure
- Lower viscosity
- Produce unsaturated bonds

Problems induced

- Thermal instability
- Incomplete combustion
- Negative environmental impact
- Clogging during pipeline transportation

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Saturation by adding H₂

- High pressure
- Availability

ADVANTAGE OF METHANOTREATING

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- The usage of cheap and abundant natural gas as the upgrading agent rather than H_2 * significantly reduces the consumption of H_2 , resulting in the notable reduction of operation cost and CO₂ emission.
- Operation pressure might be significantly lowered during methanotreating (<5 MPa), * resulting in notably reduced capital and operation cost.
- Extra liquid products will be formed due to the participation of natural gas. *
- Hydrogen might be formed as valuable byproduct, depending on the saturation degree * of cracked distillates.

CHALLENGE OF METHANE ACTIVATION



Reaction Progress

CURRENT RESEARCH STATUS

Oxidative Methane Activation



E. kondratenko, et al., ChemCatChem, 2013, 5 (3), 697

$2CH_4 + O_2 \xrightarrow{catalyst} C_2H_4 + 2H_2O$

Nonoxidative Methane Activation



$$6CH_4 \xrightarrow{catalyst} C_6H_6 + 9H_2$$

- Severe reaction conditions have to be employed to overcome activation barrier.
- Specially tailored catalyst has to be present to lower down the activation energy.
- No effective catalyst has been identified until now for methane activation.

THEORETICAL METHODOLOGY

- Methane can be more easily activated in the presence of higher hydrocarbons especially unsaturated hydrocarbons^[1] and even oxygenated hydrocarbon like alcohol^[2] and converted to liquid at temperature of 400 ~ 600 °C and atmospheric pressure.
- The synergetic effect should happen when natural gas reacts with naturally available fuels like coal, biomass, and heavy crude oil.
- The addition of steam or originally present moisture will further facilitate methane activation^[3].



¹ Choudhary, V.R.; Kinage, A.K.; Choudhary, T.V. Science **1997**, 275, 1286-1288

- ² Choudhary, V.R.; Mondal, K.C.; Mulla, S.A.R. Angew. Chem. Int. Ed. 2005, 44, 4381-4385
- ³ Ovelles, C.; Hamana, A.; Rojas, I.; Bolívar, R. Fuel, **1995**, 74, 1162-1168

ACHIEVEMENTS IN BITUMEN UPGRADING AT LAB SCALE



	Upgrading Performance and Liquid Product Properties											
Oil Sample	Viscosity (cP)	Coke Yield (wt.%)	H/C Atomic Ratio	G&D Fraction (wt.%)	Asphaltene Content (wt.%)	Density (g/cm³)	Molecular Weight (g/mol)	TAN (mg KOH/g)				
Bitumen	848,080		1.52	12.15	22.04	1.0275	700	2.59				
N ₂	2083	0.60	1.53	27.69	16.81	0.9957	527	0.51				
CH₄	1617	0.55	1.51	30.69	16.15	0.9871	541	0.24				
N ₂ + Catalyst	1276	0.86	1.58	32.47	12.32	0.9755	468	0.39				
CH₄+ Catalyst	278	0.80	1.72	43.51	9.48	0.9523	289	0.02				

Upgrading of bitumen under methane environment is technically feasible at lower pressure when suitable catalyst is charged.

Incorporation of methane molecule into carbon chain of upgraded oil was experimentally evidenced.

Compared to thermal cracking, methanotreating can obtain more upgraded oil with better quality.

A. Guo, et al., *Catal. Sci. Technol.*, (**2016**) 6, 1201; P. He, et al., *Fuel Process. Technol.*, (**2017**) 156, 290; P. He, et al., *Appl. Catal. B*, (**2017**) 201, 438; L. Zhao, et al., *Energy Fuels*, (**2016**) 30, 10330; Shen, Z., *Fuel*, (**2019**) 243, 469

ACHIEVEMENTS IN HEAVY CRUDE UPGRADING AT LAB SCALE

Oil	Upgrading Performance and Liquid Product Properties												
Sample	Coke Yield (wt.%)	Viscosity (cP @ 60 °F)	Olefin content (wt.%)	Density (API °)	Density (g/cm ³)	Asphaltene Content (wt.%)	TAN (mg KOH/g)	Stability (ASTM D4740)					
Crude A		1,203	BDL [#]	16.7	0.954	16.2	1.21	1					
Product A	0.10	56	2.4	22.8	0.916	4.2	0.85	1					
Crude B		2,249	BDL	15.6	0.961	17.7	2.09	1					
Product B	0.20	98	2.3	22.4	0.918	12.7	1.00	1					
Crude C		7,770	BDL	13.6	0.974	19.9	2.08	1					
Product C	0.50	45	1.9	19.4	0.937	10.3	0.88	1					
Crude D		89,628	BDL	12.0	0.985	24.7	3.03	5					
Product D	1.80	143	2.0	16.3	0.956	8.3	0.79	1					
Crude E		110,000	BDL	12.3	0.983	23.2	2.96	5					
Product E	0.90	658	2.1	16.1	0.957	9.3	1.05	1					

Reaction conditions: 400 °C, 30 bar CH_4 , 40 mins with 1 wt.% catalyst HOU-3

[#]Below detection limit

CATALYTIC UPGRADING OF EXTRA HEAVY CRUDE FROM PFT UNIT

Properties	PFT	PFT-P-1	PFT-P-5
Viscosity(15.6°C) /cP	125,769	185±4	109 ±5
Density (15.6°C) /g/ml	0.998	0.973	0.965
Liquid Yield / wt%	N.A.	95.4	93.3
Gas Yield / wt%	N.A.	4.0	5.54
TAN (mg KOH/g)	3.22	0.52	0.17
Olefin Content / wt%	0.054	0.152	0.342
Gasoline content /wt%	0	5.6	8.2
Diesel content /wt%	6.3	34.5	41.5
AMW / g/mol	617	400	317
Solid Content / %	0.76	0.7	0.68
Coke Yield / %	N.A.	0.15	0.80
Sulfur Content / %	4.36	2.86	1.97
Asphaltene Content / wt%	6.45	2.5	1.5



- Our technique can also effectively upgrade extra heavy crude like the one derived from paraffinic froth treatment process.
- Better upgrading performance can be achieved at lower space velocity.

Reaction conditions: 400 °C, 5 bar N_2 , 25 bar CH₄ ,1 hour with 1 wt.% and 5 wt.% catalyst

CATALYTIC UPGRADING OF VACUUM RESIDUE (VR) UNDER METHANE

Oil Sample		Upgrading Performance and Liquid Product Properties											
	Liquid Yield (wt.%)	Coke Yield (wt.%)	Viscosity (cP @ 60 °F)	Olefin content (wt.%)	Density (g/cm³@ 60 °F)	Asphaltene Content (wt.%)	TAN (mg KOH/g)						
Feed			>1 million	BDL	1.048	15.6	1.89						
Product	96.0	1.8	110	0.46	0.9615	6.5	0.64						



Complete	Upgrading Performance and Liquid Product Properties								
Samples	S Content (wt.%)	Ni Content (ppm)	V Content (ppm)						
Feed	5.53	115	220						
Product	3.02	39	65						

Vacuum residue could be largely converted into light fraction with our technique, accompanied with significantly reduced density and viscosity.

This technique will be highly beneficial and profitable for the treatment of VR and similar heavy residue.

CATALYTIC UPGRADING OF VACUUM RESIDUE (VR) UNDER METHANE

Oil Sample		Upgrading Performance and Liquid Product Properties											
	Liquid Yield (wt.%)	Coke Yield (wt.%)	Viscosity (cP @ 60 °F)	Olefin content (wt.%)	Density (g/cm³@ 60 °F)	Asphaltene Content (wt.%)	TAN (mg KOH/g)						
Feed			>1 million	BDL	1.030	15.0	2.10						
Product	98.2	0.7	177	0.45	0.9545	5.4	0.77						



Complete	Upgrading Performance and Liquid Product Properties								
Samples	S Content (wt.%)	Ni Content (ppm)	V Content (ppm)						
Feed	4.34	117	245						
Product	1.86	33	49						

Vacuum residue could be largely converted into light fraction with our technique, accompanied with significantly reduced density and viscosity.

This technique will be highly beneficial and profitable for the treatment of VR and similar heavy residue.

EFFECT OF REACTIVE GAS ENVIRONMENT UNDER BATCH MODE

			Ten	nperature (°C)		Charged catalyst		Catalyst to ratio	o oil	Gas to ratio	oil	Duration (h)			
	Con	ditions		410		HOU-2		1:100		60:1		1			
Rea	ctive			U	ogra	ding Perf	orma	nce and Lio	quid Pı	oduct Pro	opertie	S			
Gas		Viscosity (cP @ 60 °F)		Olefin con (wt.%)	tent	nt Sulfur Content (wt.%)		Density (g/cm³)	Asphaltene Content (wt.%)		TAN (mg KOH/g)		Liquid Yield (wt.%)		
Feed		587,0 @45º	00 °C	BDL		3.40	3.40 1.01002 11.6		11.6	1.	76				
Metha	ine	1,61	0	0.29		2.17		0.95766	7.43		0.74		1	98.1	
Propa	ine	750)	0.38		1.96		0.94180	6.12		0.	57	1	98.3	
Butan	e	154	Ļ	0.47		1.83		0.93701	2	4.02	0.	47		98.8	
	90	-Feed				**		Reactive Ga	as	Feed	СН	4	C₃H ₈	C₄H ₁₀	
rt.%)	80	⊷Methane						Naphtha Frac (<180 °C, wt.	tion %)	0	8.0)	8.5	10.5	
ction (w	60 50	⊷Propane ⊷Butane					Mid (`	dle Distillate F 180~360 °C, v	raction vt.%)	0	20.	0	21.0	23.7	
iss Frac	40 30						(;	Gas Oil Fract 360~500 °C, v	ion vt.%)	10.5	23.	5	24.0	25.5	
Ma	20 10						Hea	avy Residue F (>500 °C, wt.	raction %)	89.5	48.	5	46.5	40.3	
	0 0	100 200	300 T	400 500 6	00 7	00 800	А	veraged Mole Weight (g/m	cular ol)	849	49	7	485	467	
			rempe	erature (°C)											

CATALYTIC UPGRADING OF ASPHALTENE UNDER METHANE



EFFECT OF SOLVENT ON METHANOTREATING OF ASPHALTENE

DDODEDTIES	FEEDSTOCK	REA	REACTIONS		
PROPERTIES	ABA-LF ¹	R1	R2	1	
Liquid Yield ² (wt%)	N/A	89.0	89.7		
Gas Yield (wt%)	N/A	9.5	5.9		
Coke Yield (wt%)	N/A	2.3	5.3		
Overall Mass Balance (wt%)	N/A	100.8	100.9		
Asphaltene Conversion (%)	N/A	99.9	99.9	C.C.	
Methane Conversion (%)	N/A	8.5	8.6		
Sulfur Content (ppmw)	6,580 ± 40	705 ± 2	1,417 ± 26	C	
TAN (mg KOH/g)	0.27 ± 0.02	BDL	BDL	C	





Xu. H., et al., Fuel, (2021) 291, 120157

ompared to aromatic based solvent, usage paraffinic solvent can notably reduce oke formation, accompanied with better ulfur removal upon asphaltene upgrading.

Note:

1) ABA-LF means 10% asphaltene diluted with 90% solvent; R1 indicates the reaction using paraffinic solvent diluted asphaltene as the feed; R2 represents the reaction using aromatic solvent diluted asphaltene as the feed;

2) All yields are based on the total liquid feedstock mass.

Reaction conditions: batch mode; catalyst: ZHY2 at 1 wt.%; gas feed: 90% methane + 10% N₂; temperature: 400 °C; Pressure: 30 bar; duration: 1 h.

CATALYTIC UPGRADING OF DRY TSRU TAILING RESIDUE

	Reaction		CH₄+Cat		
Overall	mass baland	:e (wt%)	100.3		
Asphal	tene convers	ion (%)	93.5		
Metha	ane conversio	on (%)	1.7		
G	4.8				
C	2.7				
Lic	quid yield (wt	:%)	92.8		
Sample Initial boiling point (°C)		Final boiling point (°C)	Average molecular weight (g/mol)		
TSRU-S	129.5	735.3	627		
TSRU-S-P	122.9	488.4	242		

Upon upgrading, almost all asphaltene rich solid residue is successfully converted into high value-added light fractions

Reaction conditions: batch mode; catalyst: HOU-2 at 1 wt.%; gas feed: 90% methane + 10% N_2 ; temperature: 400 °C; Pressure: 30 bar; duration: 1 h.



ACHIEVEMENTS IN HEAVY OIL UPGRADING AT PILOT SCALE (20 L/D)

	Temperat (°C)	ure	Pressure (MPa)	WHSV (h ⁻¹)	Liqui (w	d Yield t.%)		Coke Formation Rate (g/g _{cat} -h)		Duration (h)		
Conditions	s 430		5	1	1	01		0.001	45	240		
		Upgrading Performance and Liquid Product Properties										
Oil Sample	Viscosity (cP @ 60 °F) (wt		in content (wt.%)	Sulfur Content (wt.%)		ensity g/cm³)	Asphaltene Content (wt.%)		TAN (mg KOH/g)	Stability (ASTM D4740)		
Crude	12,315			3.05		.9791		10.4	2.28	1		
Product	128		1.2	0.98	(.9430		3.1	0.43	1		
100 🖵												
8 80								wt.%	Crude	Product		
wt.		MPOK	Product	Content	Crud	e Pro	duct	Paraffins	1.3	3.4		
) 60 L	AJ-95-v2 o			(wt%)				Naphthenes	s 26.8	21.2		
				Gasoline	3	2	0	Mono-	0.0	28.3		
20			beforel	Diesel	21	3	0	aromatics	0.0	30.3		
• 0			Crude 🗑	Total	24	5	0	Bi-aromatic:	s 13.2	10.6		
0	100 200	300	400 50	0 600 7	00 80	0		Poly-	E 0			

5.3

aromatics

2.3

Distillation Temperature (°C)

ACHIEVEMENTS IN VR UPGRADING AT PILOT SCALE (20 L/D)

	VR	Product Oil						
	Feed	1-w	1-m	2-m	3-m			
Viscosity (cP @ 60 ºF)	> 1 million	187	202	207	217			
Density (g/cm³)	1.026	0.906	0.947	0.958	0.962			
Asphaltene Content (wt.%)	17.1	2.1	7.2	9.0	9.4			
Sulfur Content (wt.%)	4.10	0.64	2.45	2.81	3.00			
Nitrogen Content (wt.%)	0.63	0.14	0.27	0.44	0.51			
TAN (mg KOH/g)	1.88	0.03	0.11	0.15	0.21			
Freezing point (°C)	>50	-51	-49	-47	-48			



2-month

3-month

1-month

- The vacuum residue got significantly upgraded even after 3-month continuous run.
- The charged catalyst remains active even after 3month continuous run.

ACHIEVEMENTS IN HEAVY OIL UPGRADING AT PILOT SCALE (1 B/D)

	Temperature	Pressure	WHSV	Liquid Yield	Coke Formation Rate	Duration
	(°C)	(MPa)	(h ⁻¹)	(wt.%)	(g/g _{cat} -h)	(h)
Conditions	430	5	0.5	98	0.0017	360

01000000	Upgrading Performance and Liquid Product Properties							
Oil Sample	Viscosity (cP @ 60 °F)	Olefin content (wt.%)	Sulfur Content (wt.%)	Density (g/cm³)	Asphaltene Content (wt.%)	TAN (mg KOH/g)	Stability (ASTM D4740)	
Crude	154,730	BDL	4.08	1.0096	12.44	2.10	1	
Product	204	0.25	2.02	0.9552	5.13	0.51	1	





	Crude	Product
Naphtha Fraction (<180 °C, wt.%)	0	10
Middle Distillate Fraction (180~360 °C, wt.%)	19	34
Gas Oil Fraction (360~500 °C, wt.%)	25	27
Heavy Residue Fraction (>500 °C, wt.%)	56	29
Averaged Molecular Weight (g/mol)	616	416

ACHIEVEMENTS IN JET FUEL UPGRADING UNDER METHANE

Sample	Contents of different species (wt %)							
Name	Paraffins	Naphthenes	Olefins	Aromatics	Benzene	Toluene	E-Benzene	Xylene
Jet Fuel	53.19	14.92	1.05	30.84	0	0	0	2.74
Jet Fuel Product	21.11	15.82	1.61	61.45	2.35	9.13	2.73	12.62

Sample Name	C9-aromatics (wt%)	C10-aromatics (wt%)	C11-aromatics (wt%)	C12-aromatics (wt%)	Polycyclic- aromatics (wt%)
Jet Fuel	8.92	7.72	3.67	2.31	5.48
Jet Fuel Product	12.89	7.04	4.57	1.74	8.38

Upon upgrading, aromatics amount can be doubled with remarkable increase of BTEX, especially xylene.

Reaction conditions: continuous fixed bed mode; catalyst: HOU-2; light hourly space velocity: 2 h⁻¹; gas feed: 90% methane + 10% N₂; temperature: 400 °C; Pressure: 30 bar; time-on-stream: 6 h.

MARINE DIESEL OIL (MDO) DESULFURIZATION UNDER METHANE

Entry	Gas Yield (wt%)	l Liquid Yield ((wt%)	Coke Yield in 6 hours (wt%)	Coke Form Rate [g cok catalys	ation æ(h*g t)]	Overall Yield (wt%)	Methane conversion (%)
SC-001; CH4	2.56	96.09	1.20	0.011	L	99.85	1.81
SC-001; N2	2.82	95.40	0.96	0.008	3	99.18	N/A
Entry		Density (g/cm³, a 15.6°C)	at TAN ((mg KOH/g)	Sulfur Cor (ppn	ntent* n)	Sulfur content reduction (%)
Feed (MD	00)	0.85239 ± 0.000	02	0.24	2153 <u>+</u>	13	N/A
SC-001; C	CH ₄	0.84176 ± 0.000	02	0.03	887 <u>+</u>	<u>+</u> 1	58.8
After vaporiza	ation at 5	50 °C for possible	CS ₂ remova	ıl	636 <u>+</u>	2	70.5
SC-001;	N ₂	0.83456 ± 0.000	001	0.05	1231 <u>:</u>	<u>+</u> 9	42.8
After vaporiza	ation				1251 :	<u>+</u> 8	

Upon engaging suitable catalyst under methane environment, the quality of the MDO can be notably improved in terms of reductions of density, total acid number (close to 90%), and sulfur content (over 70%);

Reaction conditions: continuous fixed bed mode; catalyst: SC-001; light hourly space velocity: 1 h⁻¹; gas feed: 90% methane + 10% N₂; temperature: 400 °C; Pressure: 30 bar; time-on-stream: 6 h.

METHANE ASSISTED CATALYTIC DESULPHURIZATION



METHANE ROLE INVESTIGATION FOR HEAVY OIL UPGRADING



Catalyst	BET surface area (m ² g ⁻¹)	Total pore volume (mL g ⁻¹)	Micropore surface area (m ² g ⁻¹)	Micropore volume (mL g ⁻¹)
Fresh	179.8	0.205	82.7	0.043
Spent-CH ₄	88.5	0.063	36.5	0.021
Spent-N ₂	69	0.058	16.3	0.005

CH4 5 Sulfur Content (wt.%) 4.5 4 3.5 3 2.5 2 n 20 40 60 80 Asphaltene Conversion (%)

-**-**-N2

Fresh Catalyst

5.5



Spent Catalyst after N₂ run



- ✤ Methane presence effectively can suppress thermal cracking and promote desulfurization, leading to reduced coke yield and sulfur content;
- ✤ Methane presence prevent coke formation onto the internal surface due to the preferrable adsorption of methane molecules.

Spent Catalyst after CH₄ run



CONCLUSIONS

- The technical feasibility of the developed heavy oil targeted hi-grading technology is verified over various heavy feeds, and units from lab scale to pilot scale.
- The developed technology has been successfully applied to the valorization of versatile light crudes in terms of sulfur reduction, oxygen removal, TAN reduction, monoaromatics formation.
- The roles played by methane during crude upgrading process have been better understood as followings:
 - Effective suppression of thermal over-cracking;
 - > Efficacious inhibition of polymerization for coke formation.
 - Selective promotion of heavy residue conversion to light fraction;
 - Efficient prevention of heavy residue deposition/adsorption on catalyst surface, particularly internal surface through enhancing monoaromatics formation (solvent effect) and preferrable adsorption of methane molecules;
 - Novel desulfurization pathway generation through forming highly volatile sulfur containing liquid species such as CS₂ as good solvent for heavy residue dissolution;
 - Possible incorporation into the formed liquid product for liquid yield enhancement and varied properties of the upgraded oil;
 - Facilitation of deoxygenation and desulfurization reactions;

FUTURE WORK

- The heavy oil upgrading performance is in the process of being further verified at a scale of 1 barrel/d on the fabricated research prototype.
- The developed technology will be tuned to a wider spectrum of oil feed to evaluate its application generality.
- More sample characterizations will be performed to get an even better understanding of the involved catalytic reaction mechanism, beneficial for the rational design of the engaged catalyst.
- More catalysts will be synthesized to achieve optimized performance in terms of reduced viscosity, increased oil yield, and higher paraffin content.
- More model compounds will be reasonably selected to represent crude oil for better mechanistic study of the involved upgrading reactions.
- Long term stability test will be conducted at larger scale and catalyst deactivation mechanism will be better identified for its potential commercialization.



Thanks for your attention! Welcome for questions and comments



Green Catalysis Research Group (GCRG) @ University of Calgary



