



Biogas from Palm Oil Mill Effluent (POME) to Syngas for Sustainable Production of Chemicals/Fuels

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Global Greenhouse Gas Emissions

Global Greenhouse Gas Emissions by source









: 50- 75 %

CH₄

- **CO₂** : 25-45 %
- H₂S : 150-200 ppm







Trapping of Biogas at Palm Oil Mills

- All palm oil mills to have biogas trapping facilities by 2020
- National Key Economic Areas (NKEA) sector: palm oil





Biogas Plant @ FELDA Serting Hilir Mill



<u>Options for biogas</u>: 1.grid connection 2.in-house usage 3.bottling







PutraCAT

Catalysis Science and Technology Research Centre

National Key Economic Areas (**NKEA**)

NATIONAL BIOGAS IMPLEMENTATION (EPP5)



To comply with 35% GHG emission savings requirement for biodiesel under the EU Renewble Energy Directive To produce electricity for the grid connection



To convert POME to renewable energy for in-house or peripheral use

To reduce greenhouse (GHG) emissions generated from POME OBJECTIVES OF BIOGAS CAPTURE

 added revenue
 reduced carbon footprint To utilize biogas as renewable fuel to replace fossil fuel/diesel for generating steam or electricity

To produce hydrogen





Dry Reforming of Biogas $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$

Catalyst:

Noble metal catalysts:

Pt, Ru and Rh - high activity and more resistant to coke formation but very expensive and limited availability.

Ni-based catalysts:

- more suitable,
- high activity, availability and low price.
- but more sensitive to carbon deposition and difficult to prevent sintering of nickel.











Physical Properties of Samples

Support/ Catalysts	Chemical Composition ^a			Surface Area	Bulk density	
	Si	Ce	Ni	(m²/g)⁵		
SiO ₂	n.a.	n.a.	n.a.	408	0.47	
CeO ₂ -SiO ₂ (CS)	n.a.	n.a.	n.a.	232	0.36	
Ni/CS-S	47.29	20.53	31.75	226	0.36	
Ni/CS-D	45.60	20.61	33.53	304	0.51	
NiCo/CS-S	36.92	15.43	23.47	224	0.32	
NiCo/CS-D	38.24	14.57	22.73	286	0.62	
NiPt/CS-D	43.17	19.46	28.30	384	0.49	

S – Sequence

n.a = . not analyzed

^a Investigated by XRF (Surface Analysis)

D - Direct

^b Calculated by BET equation



Morphology: SEM





- The morphology of SiO₂ changed significantly after CS preparation
- The particle of SiO₂ of Ni/CS-D relatively larger than that of Ni/CS-S
- The morphology depend on the preparation method of sample used.

SEM images of catalysts





Crystallographic : XRD



Between Ni/CS and NiCo/CS

- Mainly the patterns were almost similar, but the NiCo/CS either prepared by sequence or direct method showed lower NiO peaks than Ni/CS and an additional peak of NiCo₂O₄
- This indicates that the combination of Ni and Co metal has change the crystallinity
- NiPt/CS-D showed no significant different to Ni/CS due to very low content of Pt

XRD patterns of calcined catalysts





XRD patterns of reduced catalysts

Sample	CeO ₂ ª (nm)	NiO ^ь (nm)	Ni ^c (nm)	
Ni/CS-S	8.07	10.63	14.96	
Ni/CS-D	5.53	8.94	13.39	
NiCo/CS-S	7.16	9.30	14.85	
NiCo/CS-D	5.47	8.03	12.75	
NiPt/CS-D	6.08	9.80	12.82	

Crystalline particle size

- XRD patterns showed that Ni metallic phase formed after reduction process
- The Ni particles are relatively small of around 13-15 nm. The differences are due to the different method used









TEM images of selected reduced catalysts



*Reducibility: H*₂-*TPR*





H₂-TPR profiles of catalysts

 The figure shows various reduction profiles. Different method of catalyst preparation gave different profiles

 An additional peak at 325 and 295 °C was ascribed as the reduction of cobalt oxide.

Reduction peak > At around 400 °C \rightarrow Reduction of NiO > At > 700 °C \rightarrow Reduction of CeO₂





Catalytic Evaluation

Catalyst activities over all catalysts



Catalytic performance of catalysts as a function of time at GHSV 3000 $ml/g_{cat}h$ (a) CH₄ conversion and (b) CO₂ conversion





Carbon formation analysis: TGA



TGA profiles of spent catalysts under O₂ flow

The spent catalysts

- Catalyst with lower amount of mass loss, indicating lower carbon formation
- NiPt/CS-D gave low carbon formation due to the existence of Pt





Carbon formation analysis: SEM



SEM images of spent catalysts





















Direct cracking methane to hydrogen and carbon.

 $(CH_4 \rightarrow 2H_2 + C)$ over a Ni supported catalyst provides a clean method of producing CO_x free **Hydrogen** and **Carbons** (Nanotubes, Microfibers, Microballs).

Using Cu/Co catalyst - produced Graphene

Graphene material for storing hydrogen at room temperature. The novel form of engineered graphene has exhibited a hydrogen storage capacity of 14% by weight at room temperature, exceeding the capacity of current materials. (Rensselaer Polytechnic Institute)

US DOE has set a gravimetric storage target for vehicular on-board hydrogen storage (for the entire system, not just the material) of 6% wt. by 2010 and 9% wt. by 2015





Catalytic Conversion of CO₂ to Liquid Products

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- Global warming and climate change are attributed to the increasing carbon dioxide (CO₂) concentration in the atmosphere.
- The concentration of CO₂ in the atmosphere consequently increased from 280 ppm before the industrial revolution to 407 ppm in July, 2017. It was predicted to reach 570 ppm by the end of the century.
- Thus, various strategies for the separation, capture, storage, and conversion of CO₂ have been developed to reduce atmospheric CO₂ concentration.





Global Carbon Emissions from Fossil Fuels, 1900-2014













- Of these strategies, CO₂ utilization is the most promising alternative because not only it can reduce CO₂ concentration but also it can convert CO₂ into C1 valuable products, such as methanol (CH₃OH), formic acid (CHOOH), carbon monoxide (CO), and methane (CH₄).
- Meanwhile, although CO₂ utilization has been explored for centuries, the catalytic conversion of CO₂, such as hydrogenation reaction, offers challenging opportunities for energy sustainability and the environment.





Fischer-Tropsch Catalyst: Preparation and Behavior during Catalytic Reaction





Introduction: XGL Technology



Introduction: Gasification



Introduction: Syngas process



Introduction: Fischer-Tropsch Synthesis



Introduction: Fischer-Tropsch Synthesis



Franz-Fischer

Han Tropsch

History of founder Fischer-Tropsch

 Kaiser-Wilhelm Institute of Coal Research in Mülheim an der Ruhr
 1920s
 Coal derived gas
 Objective : To produce hydrocarbon
 Commercialized in 1930s

Introduction: Fischer-Tropsch



Fischer-Tropsch (F-T) was designed in 1920 by <u>Franz Fischer</u> and <u>Hanz Tropsch</u> in Germany.

□ The F-T process is a <u>chemical reaction</u> that convert a mixture of <u>carbon monoxide and</u> <u>hydrogen</u> into <u>liquid hydrocarbons</u>

□ It is a process of <u>converting gas to liquid</u>, in which the H₂ and CO typically derived from coal, natural gas or biomass

 $\frac{CH_4 + H_2O \rightarrow 3H_2 + CO}{C + H_2O \rightarrow H_2 + CO}$



□ The F-T process is focused as one of the source of <u>low-sulfur diesel</u> fuel and address the <u>supply of petroleum-derived carbon</u>.

Introduction: Reaction process

□ In the F-T process, the CO and H₂ in the syngas are converted into hydrocarbon of various of molecular weights according to the following reaction

 $(2n+1)H_2 + n CO \rightarrow C_nH_{(2n+2)} + n H_2O$

There are other <u>side reactions</u> which also taking place in the process, among it, the water-gas-shift reaction is important



Introduction: Catalyst

The discovery of the 'gasoline synthesis' by Fischer and Tropsch published in 1926 related to iron and cobalt as catalysts, both the metals remaining until today the only ones for industrial application.

□ The use <u>cobalt-based catalyst is advantageous</u> as cobalt is highly resistant from water inhibition unlike iron-based catalyst [1]

□ <u>Nickel</u> also a typical FT catalysts, which <u>capable for producing higher molecular weight</u>

"Optimizing the surface area and porosity is often the key to improving the catalytic performance"



Unsupported catalyst rapidisplating catalyst: therma

<u>Carbon is highly</u> <u>Effective</u>

- Neutrality (carbon): less coke formation.
- High surface area and large porosity: allow of reactant.







Promotion of <u>nickel-cobalt</u> supported <u>walnut-</u> <u>shell</u> derived carbon catalysts for Fischer-Tropsch reactions



OBJECTIVES

- i) To synthesis and characterize Ni and Co supported on walnut shell derived activated carbon
- ii) To study the effect of Ni and Co dopants on F-T process
- iii) To investigate the effect of reaction condition: pressure and temperature in product distribution and CO₂ conversion

Promotion of nickel-cobalt support walnut-shell derived carbon catalysts for Fischer-Tropsch reactions *(Reactor)*

Method : F-T Catalytic Reaction

1. F-T catalytic activity was tested <u>and</u> GC-TCD

in a stainless steel <u>fixed bed reactor</u> (FBR)

2. The catalyst (<u>oxide phase</u>) initially was <u>reduced</u> to <u>metallic phase</u> under 5% of H_2 in Argon at 500 °C (10 cc/min) in FBR reactor

3. The F-T reaction directly started after <u>lowering the temperature of FBR reactor</u> to desired reaction temperature and reactant gases (CO, H_2 , N_2) with ration <u>3:6:1</u> were continuously flow (10 cc/min)



Schematic diagram of the FBR reactor

Promotion of nickel-cobalt support walnut-shell derived carbon catalysts for Fischer-Tropsch reactions (Catalyst Characterization)



- Single metal oxide support AC catalyst (Co/AC) exhibited the present of Co₂O₃ phase at 2θ: 36.5°, 42.5°, 61.5° and 74°, while Ni/AC exhibited NiO phase at 2θ values of 51.5° and 76°
- □All the xNiyCo/AC catalyst showed formation of mixed oxide phase



□ $\underline{Ni/AC}$ showed reduction at temperature 279°C and 593°C : 1ST reduction-> decomposition of nitrate 2nd reduction -> $\underline{NiO} \rightarrow$

<u>Ni°</u>

Promotion of nickel-cobalt support walnut-shell derived carbon catalysts for Fischer-Tropsch reactions (Catalytic F-T Activity)

□All of the catalysts resulted in formation <u>gasoline</u>, <u>diesel and wax</u>

- F-T activity catalysed by Ni and Co with concentration
- i) 10%Co:5%Ni
- ii) 5%Co:10%Ni
- iii) 7%Co:7%Ni (same weight ration of Co and Ni)
- □ It can be summarized that $\frac{7C07Ni}{A}C$ <u>catalyst</u> <u>favour gasoline (C₅-C₁₁)</u> formation which due to the highest reducibility potential
- The high reducibility of the catalyst enabled it to have more <u>active metal sites</u>, which in turn affected the CO conversion and gasoline fraction production positively



Promotion of nickel-cobalt support walnut-shell derived carbon catalysts for Fischer-Tropsch reactions (Effect of F-T Temperature & Pressure)



- CO conversion increased from 65%
- (1 bar) to 84 % at elevated



Catalytic Conversion of Carbon Dioxide into Liquid Fuel at Low Temperature

• Hydrogenation reaction $CO_2 + H_2 - HCOOH \Delta H = -31.5 \text{ kJmol} - 1 \dots (1)$ $CO_2 + 3H_2 - CH_3OH + H_2O \Delta H = -49.6 \text{ kJmol} - 1 \dots (2)$

- Fischer-Tropsch process CO + 2H₂ $-CH_3$ OH ΔH = -90.8 kJmol⁻¹ ...(3)
- CO steam reforming
- $CO + H_2O = HCOOH \Delta H = 72.7 \text{ kJmol}^{-1} ...(4)$

- Synthesis of the catalysts using sol gel method
- Catalysts characterization
- Catalysts performance
 - Reaction time
 - Reaction temperature
 - Solvent & condition
- Products analysis- HPLC



Reactor

- The prepared catalysts were characterized using several techniques.
- Results showed a good indication of catalysts properties to be a good heterogeneous catalysts in hydrogenation of CO₂.
- It can be divided into several properties such as surfaces, crystallinity and morphology.

Table 1. Surface properties using BET method

Properties	Catalysts			
	Al ₂ O ₃	PdNi-Al ₂ O ₃	AgNi-Al ₂ O ₃	
BET Specific surface area (m²/g)	154.4	19.28	12.35	
Micropore Area (m ² /g)	2.42	8.41	7.23	
Pore Size (nm)	6.8	12.8	10.12	
Micropore Volume (cm ³ /g)	0.002	0.004	0.003	
External Surface Area (m ² /g)	65.31	10.87	8.96	





PdNi/Al ₂ O ₃	Temp (°C)	CO ₂ : H ₂ (Bar)	Time (h)	Solvents	Base addition	[FA] (mg/L)
Pd-Ni	130	10:25	6	1,4-Dioxane	-	79.90
Pd-Ni	130	10:25	4	1,4-Dioxane	-	65.77
Pd-Ni	130	10:25	2	1,4-Dioxane	-	23.45
Pd-Ni	130	10:20	6	1,4-Dioxane	-	77.06
Pd-Ni	130	10:10	6	1,4-Dioxane	-	14.90
Pd-Ni	130	10:25	6	DMSO	-	2.7
Pd-Ni	130	10:25	6	1,4-Dioxane	Et ₃ N	13.30
AgNi/Al ₂ O ₃						
25Ag-Ni	130	10:25	6	1,4-Dioxane	-	48.37
20Ag-Ni	130	10:25	6	1,4-Dioxane	-	13.66
15Ag-Ni	130	10:25	6	1,4-Dioxane	-	33.22
10Ag-Ni	130	10:25	6	1,4-Dioxane	-	46.00
5Ag-Ni	130	10:25	6	1,4-Dioxane	-	45.71
5Ag-Ni	130	10:25	6	DMSO	-	NR





• **Condition:** Pressure ratio (CO₂:H₂)= 10:25, Reaction time: 6h, Solvent: 1,4-Dioxane



Cycle	FA Yield (mg/L)	TON	TOF
1	79.9	2.18	10.1X10 ⁻⁵
2	78.4	2.14	9.91X10 ⁻⁵
3	75.2	2.05	9.49X10 ⁻⁵
4	71.6	1.95	9.03X10 ⁻⁵

* Reaction carried out at 130 °C, 0.2g of PdNi/Al₂O₃, CO₂:H₂ pressure ratio of 10:25 bar, 6 hours

• No significant loss of catalyst performance with approx. 10% loss after 4 time cycles



• Ion Formate would be formed in the presence of catalyst and proceed further reaction to form formic acid. It was confirmed by Ion Chromatography (IC) and showed the presence of small amount of formate around 15ppm.



- CO₂ hydrogenation at lower temperature compared with other conventional method.
- Reaction carried out in autoclave reactor at temperature ranging of 100-145 °C in the presence of Pd and Ni based catalysts. The presence of Ag species was deactivated the Ni activity.
- A small amount of methanol was detected at higher reaction temp. of 145 °C.
- At optimum condition of H₂:CO₂ pressure ratio of 25:10 bar at 130 ºC, reaction time of 6 h, it was successfully converted ~40% CO₂ into liquid product namely formic acid.
- The potential of this work can reduce the energy consumption during CO₂ conversion reaction, overcome the hydrogen storage issues and utilize the waste CO₂ into other valuable products in the future.







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Thank you

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