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Enhanced Syngas Production from Waste Lubricant Oil Reforming with Transition Metal Catalysts

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Abstract This research focuses on the utilization of waste lubricant oil (WLO) from motor vehicles, machinery, and industrial sector. Usually, most WLO is still subjected to incineration or landfill which led to environmental problems from air pollution to heavy metal contaminated water and soil. However, WLO can be recovered as renewable fuel because of its exceptionally high carbon content. Its calorific value may be retrieved by thermochemical techniques i.e., catalytic steam reforming for synthesis gas production. Here, steam reforming of WLO was performed in a micro fixed-bed reactor at atmospheric pressure with catalytic upgrading to improve the quality of product and hydrogen yield. The effects of ER and metal (Ni and Fe) loadings on dolomite and olivine supported catalysts prepared by impregnation method were investigated. Results showed that the product gas of high CH_4 and CO_2 was obtained for case of Fe and Ni/olivine. In contrast, 5%Ni/dolomite exhibited superior overall activity with the highest conversion and hydrogen yield. In this case, hydrogen and carbon conversions were 65.71% and 66.38%, respectively while H_2 to CO molar ratio was 1.05 and the lower heating value was 6.76 MJ/m^3. It can thus be suggested that surface-active site of Ni on dolomite has high activity for C-C cleavage and water gas shift reaction. The conversion to H_2 and CO was improved through methane and hydrocarbon steam reforming on the catalyst surface. Catalytic reforming of WLO not only enhanced synthesis gas and H_2 which can be readily used as energy, and partial source of H_2, but also as appealing sustainable and economic waste management option.

Introduction

Waste Lubricant Oil (WLO)

- 230 million liters per year in Thailand
- High hydrocarbon content, heating value
- High viscosity, contaminated with heavy metals and PAHs

Steam reforming

- High temperature to convert carbonaceous raw materials into fuel gas
- Upgraded product to syngas
- Low cost for hydrogen production
- PAHs ➔ Aliphatic compounds
- Heavy metals ➔ Ash, simpler to manage as solid phase.

Catalytic Reforming

- Highly effective
- High resistance and low price
- Enhance water-gas shift reaction and hydrogenation
- Degrade aromatic hydrocarbon structure

Objective: Investigate the effects of ER and catalyst (Ni and Fe) loadings on dolomite and olivine supports to improve both quality and quantity of fuel gas from steam reforming of WLO.

Materials and methods

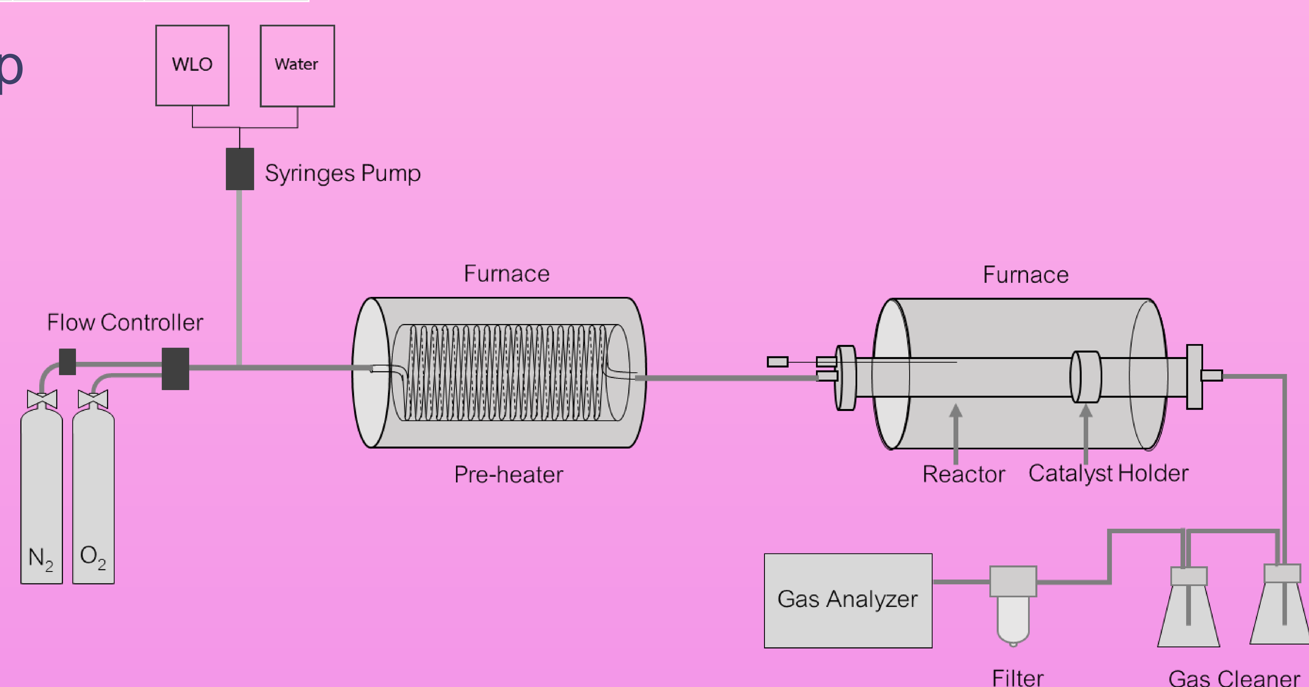
Fresh and used oils analysis

Proximate Analysis (wt.%)	Fresh	Used
Moisture	0.25	0.10
Ash	0.02	0.43
Volatile organic content	97.68	96.75
Fixed carbon	1.88	2.72
LHV, (MJ/Kg)	45.05	42.16
Ultimate Analysis (wt.%)		
Carbon	84.50	84.19
Hydrogen	14.32	13.39
Nitrogen	0.31	1.02
Sulfur	0.21	0.49
Oxygen*	0.66	0.91

Used oil heavy metals		
Fe	mg/kg	5.6
Pb	mg/kg	0.28
Cr	mg/kg	2
Cu	mg/kg	12
Ni	mg/kg	0.11
Zn	%wt.	919
Mo	%wt.	765

Experimental set-up

- **Equivalent ratio (ER)** **0.88, 1.00, 1.04**
- **5%, 10% Fe on olivine or dolomite**
- **5%, 10% Ni on dolomite**



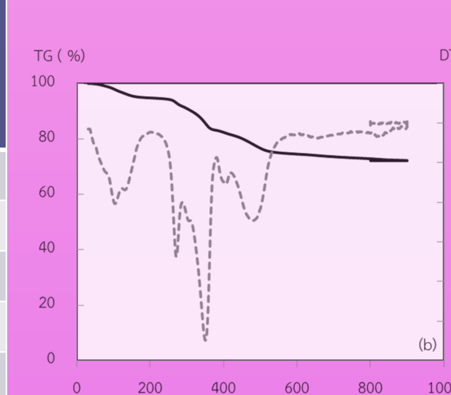
Characterization of catalysts

Surface area

Catalysts	S_{BET} (m^2/g)	V_t (cm^3/g)	Pore diameter (nm)
5%Fe/olivine	1.29	0.0088	32.07
10%Fe/olivine	2.13	0.0142	31.44
5%Fe/dolomite	5.49	0.0242	21.52
10%Fe/dolomite	4.97	0.0245	24.19
5%Ni/dolomite	19.77	0.0923	3.93
10%Ni/dolomite	12.18	0.0818	2.65

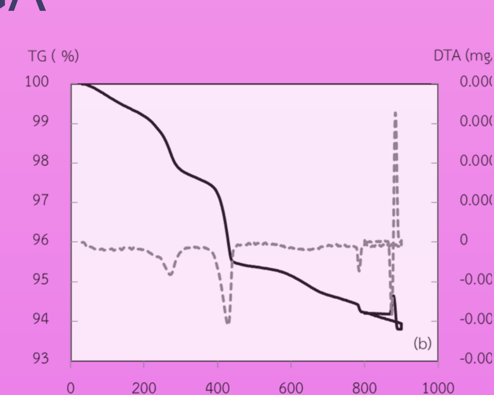
TGA

Before



5%Ni/dolomite

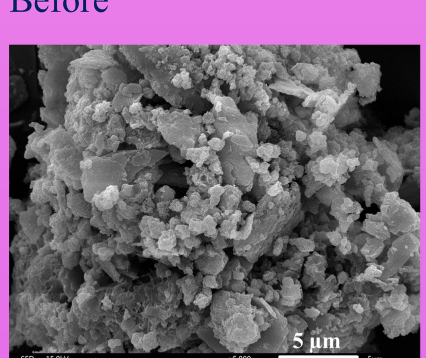
After



5%Ni/dolomite

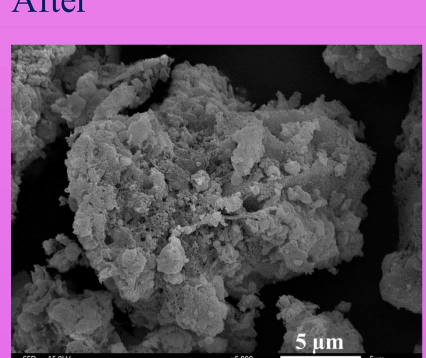
SEM

Before



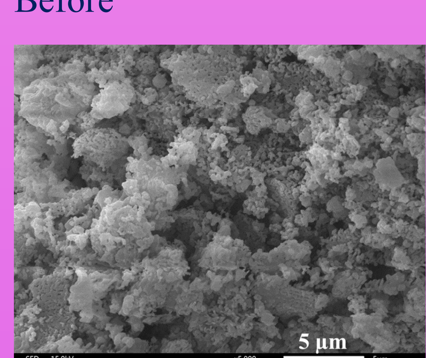
5%Ni/dolomite

After



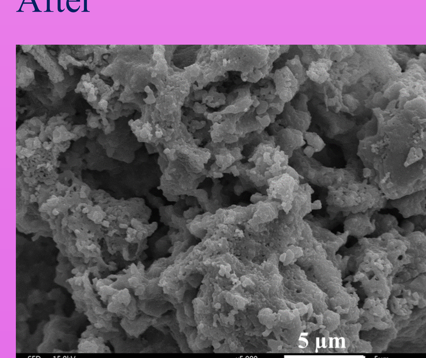
5%Ni/dolomite

Before

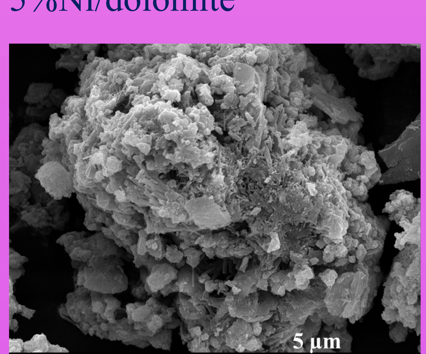


5%Fe/dolomite

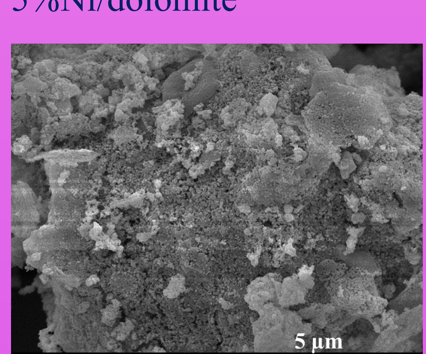
After



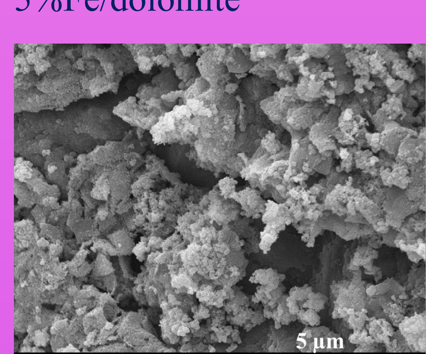
5%Fe/dolomite



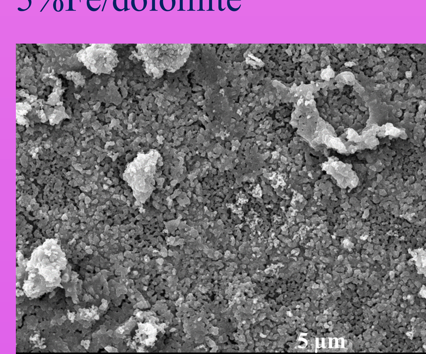
10%Ni/dolomite



10%Ni/dolomite



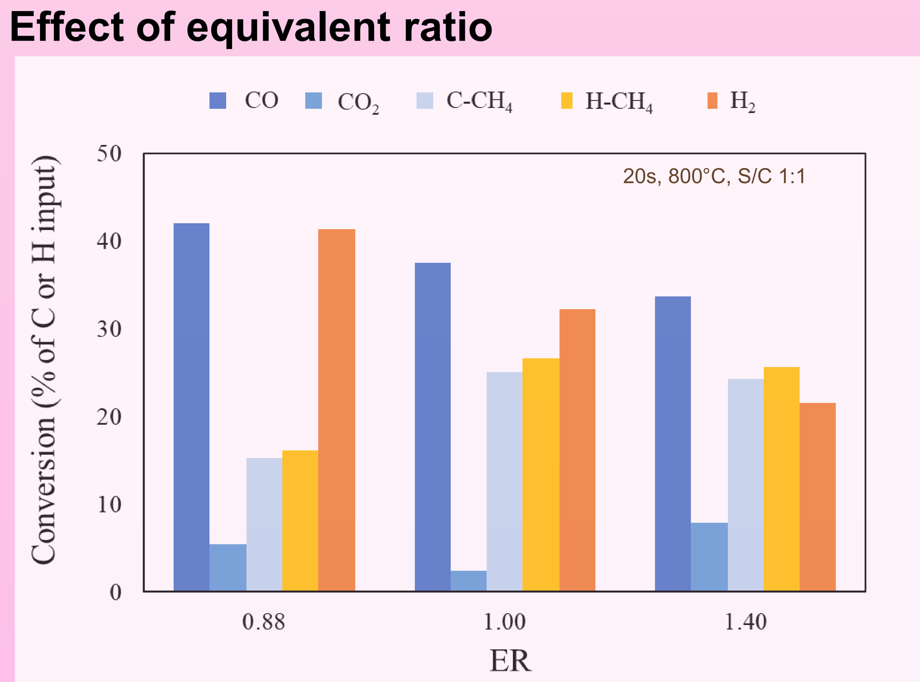
5%Fe/olivine



5%Fe/olivine

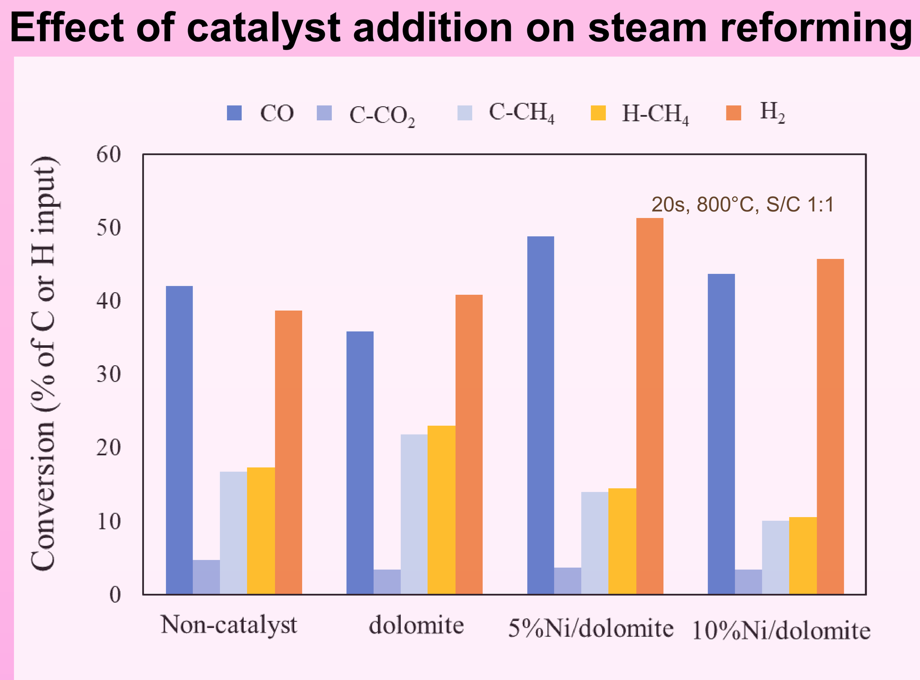
Results and discussion

Effect of equivalent ratio



- Higher in ER from 0.88 to 1.40
  - H_2 and CO conversions decreased
  - CH_4 conversion increased
- ER 0.88 is optimal for high C and H conversions
  - C-Conversion 62.76%
  - H-Conversion 57.47%

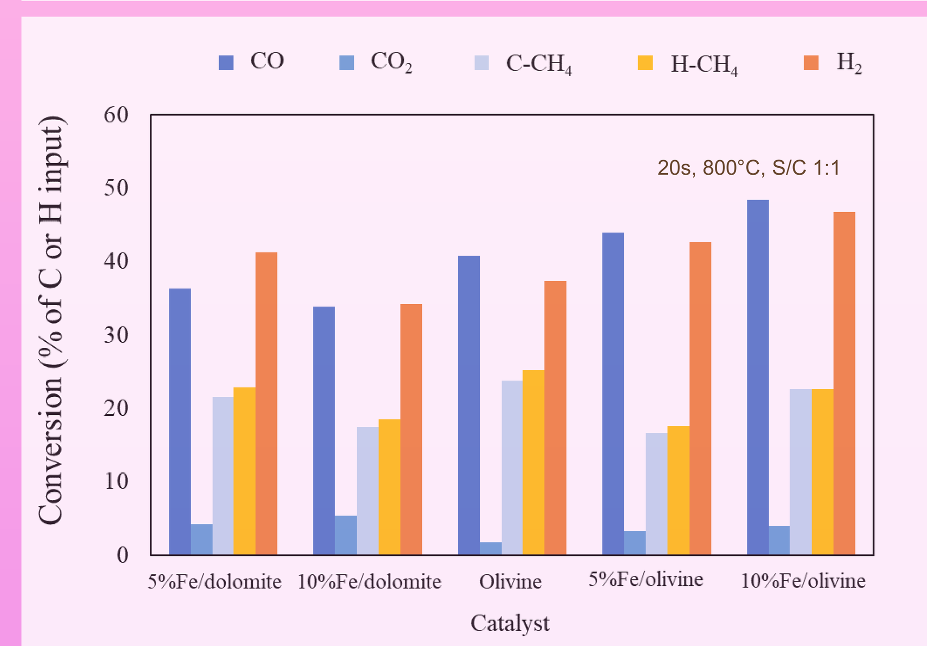
Effect of catalyst addition on steam reforming



- Lower %Ni on dolomite from 10 to 5%
  - H_2 and CO conversions increased
- Optimal at 5%Ni/dolomite
  - CO-Conversion 48.78%
  - H_2-Conversion 51.31%

5%Ni/dolomite > 10%Ni/dolomite> dolomite

Water-gas	$C + H_2O \leftrightarrow CO + H_2$
Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$
Boudouard	$C + CO_2 \leftrightarrow 2CO$



- Lower %Fe on dolomite from 10 to 5%
  - H_2 and CO conversions increased
- Higher %Fe on olivine from 5 to 10%
  - H_2 and CO conversions increased
- Optimal at 10%Fe/olivine
  - CO-Conversion 33.86%
  - H_2-Conversion 34.15%

10%Fe/olivine > 5%Fe/olivine > olivine

LHV, Cold gas efficiency, H_2/CO

Catalysts	Non - Catalyst	Dolomite	5%Ni/ dolomite	10%Ni/ dolomite	5%Fe/ dolomite	10%Fe/ dolomite	Olivine	5%Fe/ olivine	10%Fe/ olivine
LHV (MJ/m^3)	5.65	6.45	6.76	5.42	6.45	5.45	5.65	6.28	6.57
Cold gas efficiency (%)	73.69	84.10	88.15	70.67	84.10	70.98	73.65	81.81	85.58
H_2/CO	0.92	1.14	1.05	1.04	1.14	1.01	0.92	0.97	0.97

Conclusions

- ER has prominent effect on carbon and hydrogen conversions.
- 5%Ni/dolomite has the highest pore volume and surface area resulting in high conversion.
- Ni catalysts significantly increase the efficiency of HC conversion to syngas.
- CaO and MgO in dolomite, with their CO_2 capture potential, exhibit effective deoxygenation reaction resulting in high favorable syngas generation selectivity.
- Robust catalyst is 5%Ni/dolomite which improved carbon conversion to 66.38% and hydrogen conversion to 65.71% when compared with non-catalyst case.
- WLO reforming is an effective waste management technique, diverting otherwise landfill disposal to produce alternative fuels and valuable products for chemical feedstocks.

Acknowledgements

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