UNIVERSITI PUTRA MALAYSIA

AGRICULTURE • INNOVATION • LIFE

# The Palm Oil Milling Technology Exhibition & Conference (POMtec) 2023

## BIOLUBRICANT AND GREEN DIESEL PRODUCTION FROM BIOWASTE DERIVED FROM PALM OIL INDUSTRY

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# Palm Free Acid Distillate (PFAD)

- ❑ Malaysia's total oil palm planted area has reached 5.67 million hectares, with total CPO production of 18.45 million tonnes in year 2022, [MPOB].

- ❑ PFAD is generated in about 5% of the amount of CPO used. [Jumaah et al., 2019].


~ 922,500 tonnes / year 2022

- ✓ Composition: 81.7 % FFA, 14.4% glycerides etc. [J.E. Lam et al., 2022].

- ✓ Selling price : RM 4,313.50/tonne (Year : 2022.) (MPOB) (FOB)

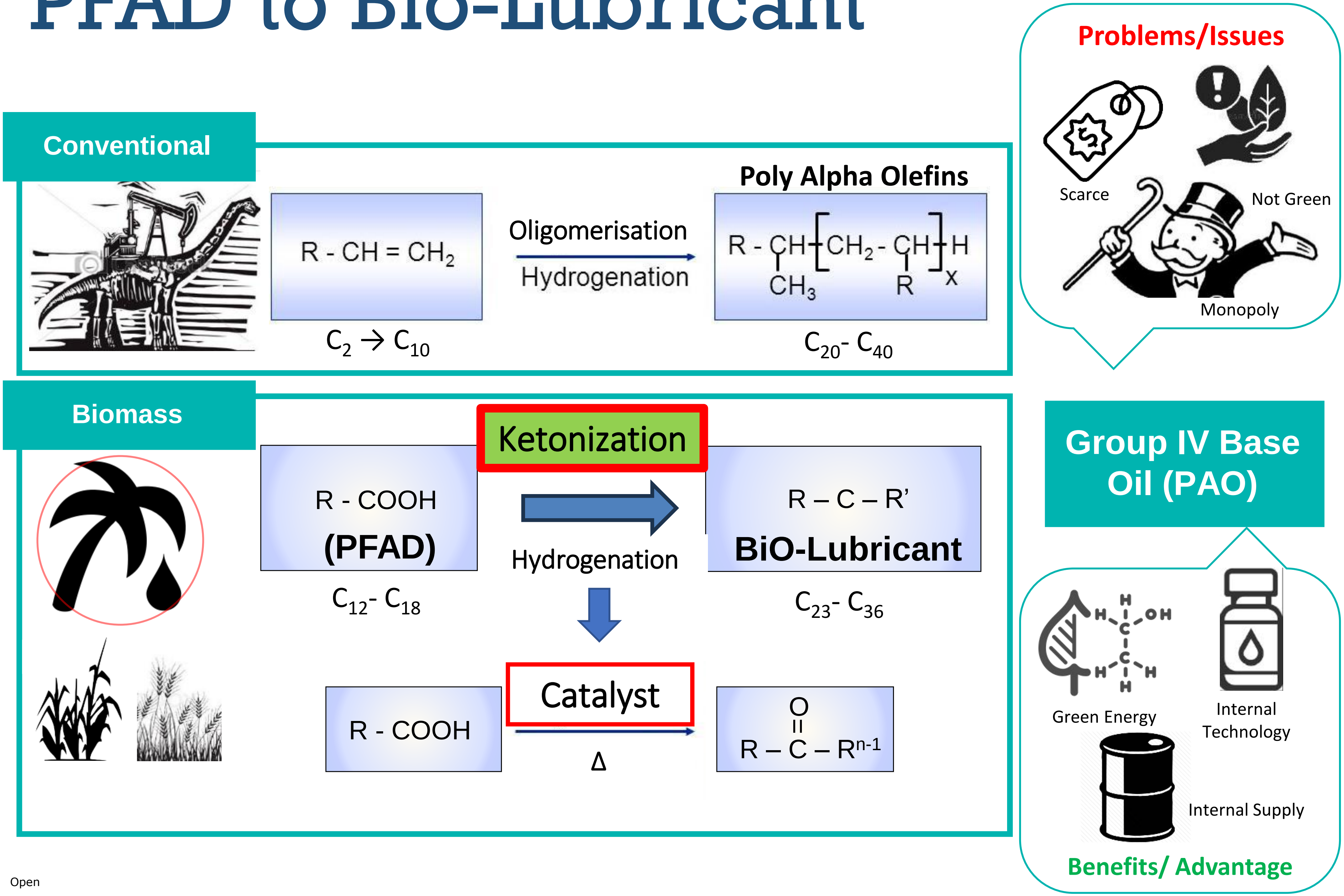




**PFAD as a Feedstock**

- **BiO-Lubricant Intermediates (Bio-Wax)**
- **Green Diesel / Bio-Jet Fuel**

# PFAD to Bio-Lubricant



# Ketonisation reaction products

**PFAD/ Palmitic acid**


**BiO-Wax** ($C_{31}H_{62}O$)

**Conversion : 92.3%**
**Yield : 27.7%**

Intermediate products (Palmitone)


**BiO-Lubricant**

**Speciality Chemicals**

Ketonization: $2C_{15}H_{31}COOH \rightarrow C_{31}H_{62}O + CO_2 + H_2O$ [1]

Decarboxylation: $C_{15}H_{31}COOH \rightarrow C_{15}H_{32} + CO_2$ [2]

Decarbonylation: $C_{15}H_{31}COOH \rightarrow C_{15}H_{30} + CO + H2O$ [3]

Thermal Cracking: $C_{15}H_{31}COOH \rightarrow Lighter\ HC's + CO_2 + H_2O + CO$ [1]

# PFAD to **Green Diesel**


**First generation Biodiesel:** fatty acid or fatty acid monoalkyl ester. (FAME)

- Low combustion value
- High freezing point
- Chemical instability
- Restricted Usage scenarios

**Second generation Green Diesel / HVO:** Diesel-Like hydrocarbon

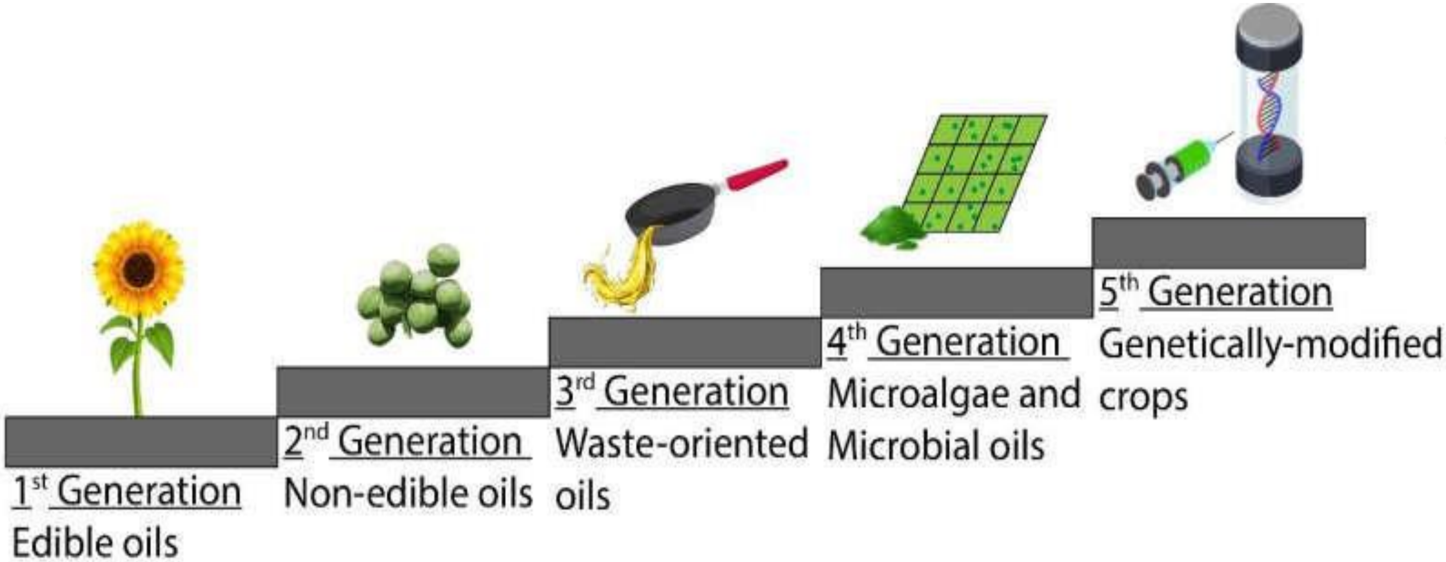
It is a hydrocarbon produced by the removal of oxygen and part of carbon, and its structure and composition are similar to that of petrochemical diesel oil.

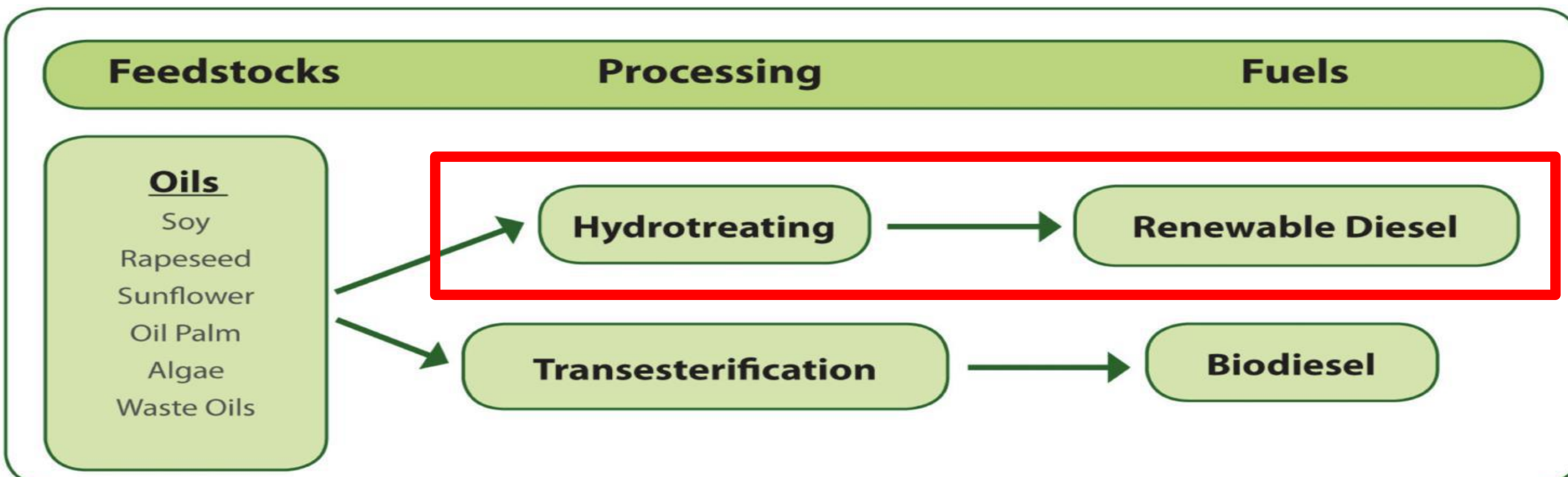
**Advantages:**

- ✓ Energy saving;
- ✓ Consumption reduction;
- ✓ More adequate combustion;
- ✓ Wide applicability;
- ✓ Strong climate adaptability.

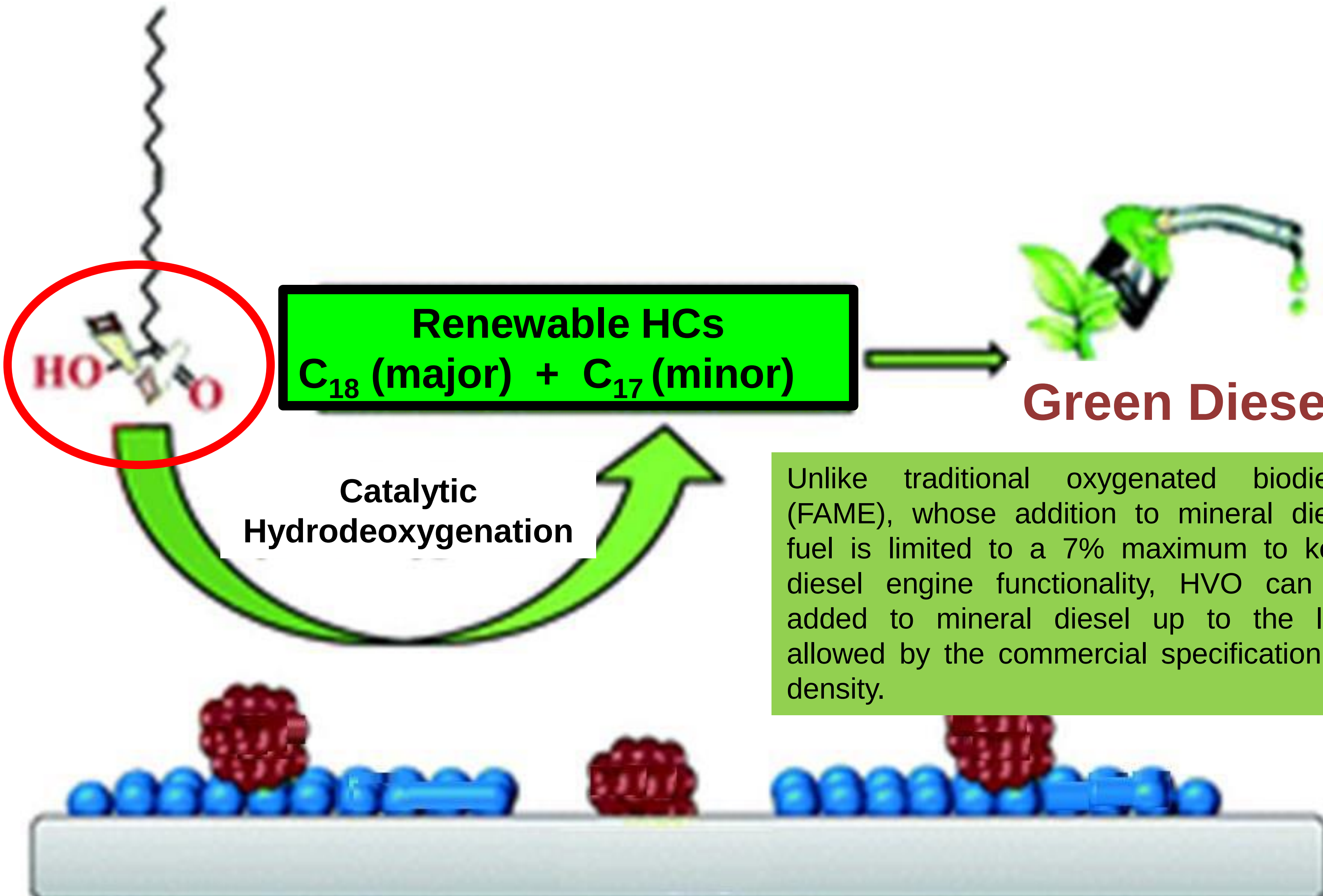
# What is Green Diesel ?

- ✓ **Second generation of Biofuel, which has a similar molecular structure as petroleum diesel but provides better diesel properties.**



# Hydrodeoxygenation Reaction




Unlike traditional oxygenated biodiesel (FAME), whose addition to mineral diesel fuel is limited to a 7% maximum to keep diesel engine functionality, HVO can be added to mineral diesel up to the limit allowed by the commercial specification on density.

# BACKGROUND- Application of Heterogenous Catalysts

**Disadvantages**

**Common Deoxygenation catalyst**

- Noble metal--Pd, Pt ← Too expensive
- Sulphide ← Pollute the environment
- Nitrates, Phosphide ← Complex preparation process
- **Cheaper metal--Ni**

**Metal Organic Framework (MOF)**

- **IRMOF series materials**
- **ZIF series materials**
- **CPL series materials**
- **MIL series materials**
- **PCN series materials**
- **UiO series materials**

**-This Investigation-**
**MOF Based Catalyst**

**MIL-101-Cr advantages**

**Materials of institute Lavoisier frameworks (MIL)**

→

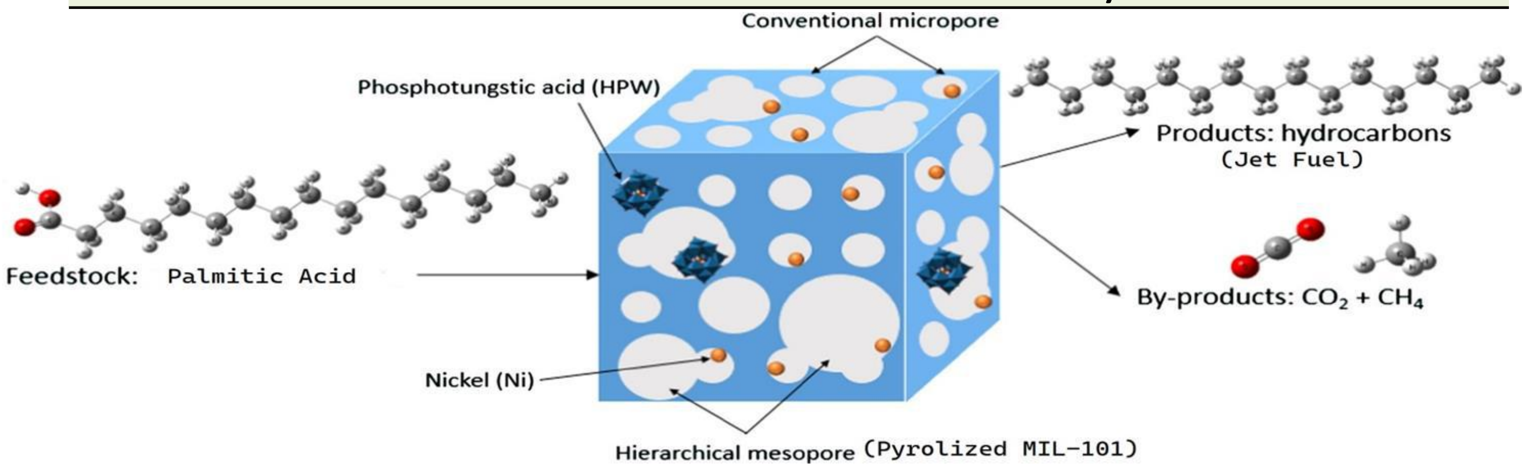
- **Well-ordered tunable porous system.**
- **High hydrothermal-chemical stability.**
- **Carrying the original Lewis acidity by the unsaturated metal ions.**

[5] A. Dhakshinamoorthy, M. Alvaro, A. Corma and H. Garcia, Dalton Trans., 2011, 40, 6344–6360.

# Hydrodeoxygenation(HDO) Reaction

**Hydrodeoxygenation (HDO)** is a hydrogenolysis process for <u>removing oxygen from oxygen-containing compounds</u>.

| Reaction | Hydrodeoxygenation (HDO) |
|---|---|
| Product | **n-paraffins**, CO, $CO_2$, water |
| Molecular species | No existence $O_2$ species |
| Cetane number | High cetane number (80-90) |
| Performance | High fuel performance |
| Flash point level | Low flash point |
| NOx emission | Lower NOx emission than Biodiesel |
| Feed sensitivity | Not sensitive with FFA content |
| Economic level | Economically effective |



# Methodology- catalyst preparation

## 1.1. The preparation of MIL-101-Cr

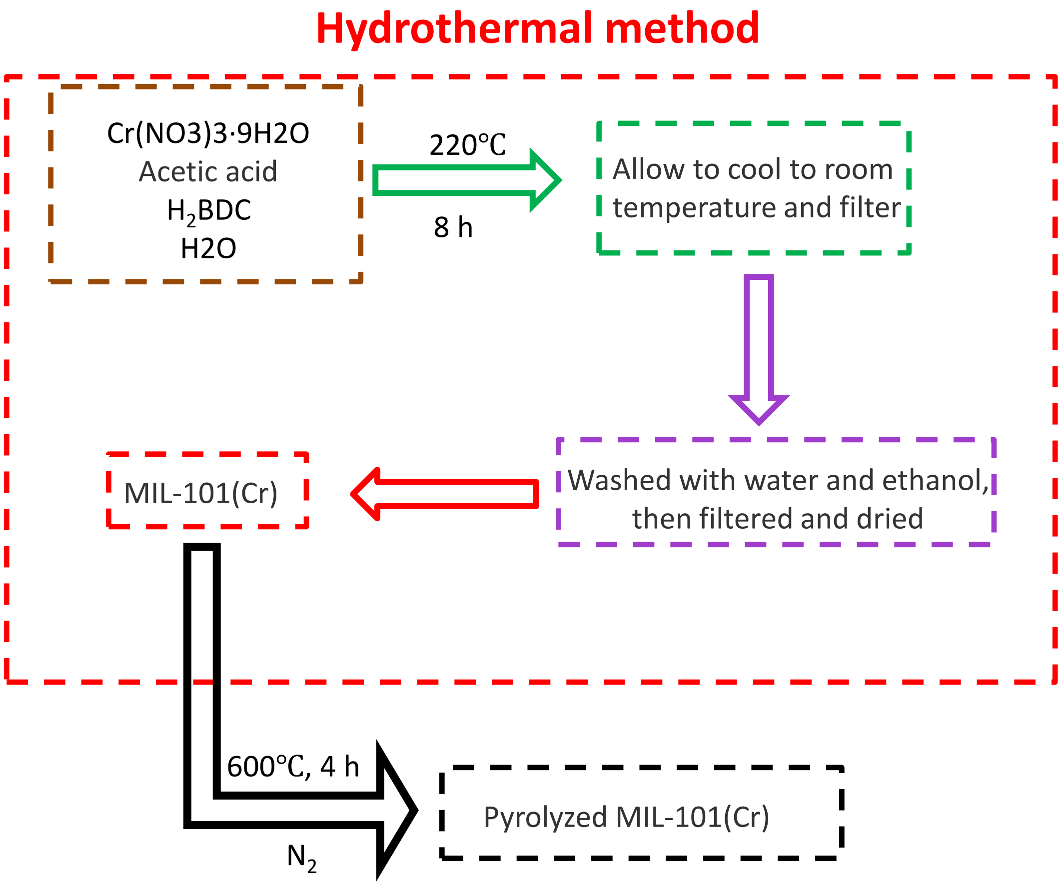



Figure. The preparation process of MIL-101-Cr and P-MIL-101-Cr

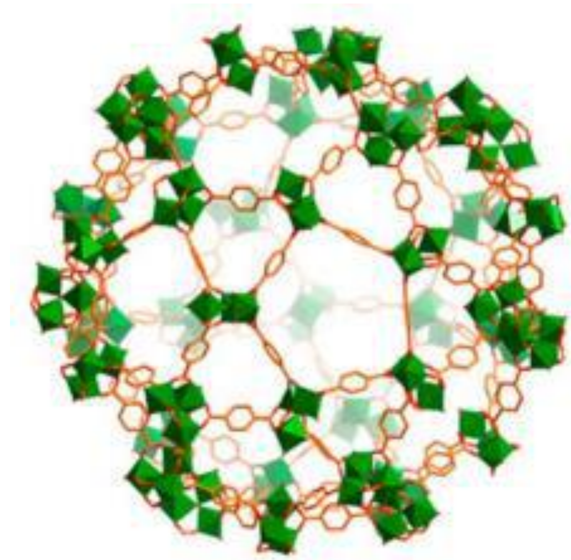


Fig. The structure of MIL-101-Cr

# Methodology- catalyst preparation

## 1.2. The preparation of P-Ni/MIL-101-Cr

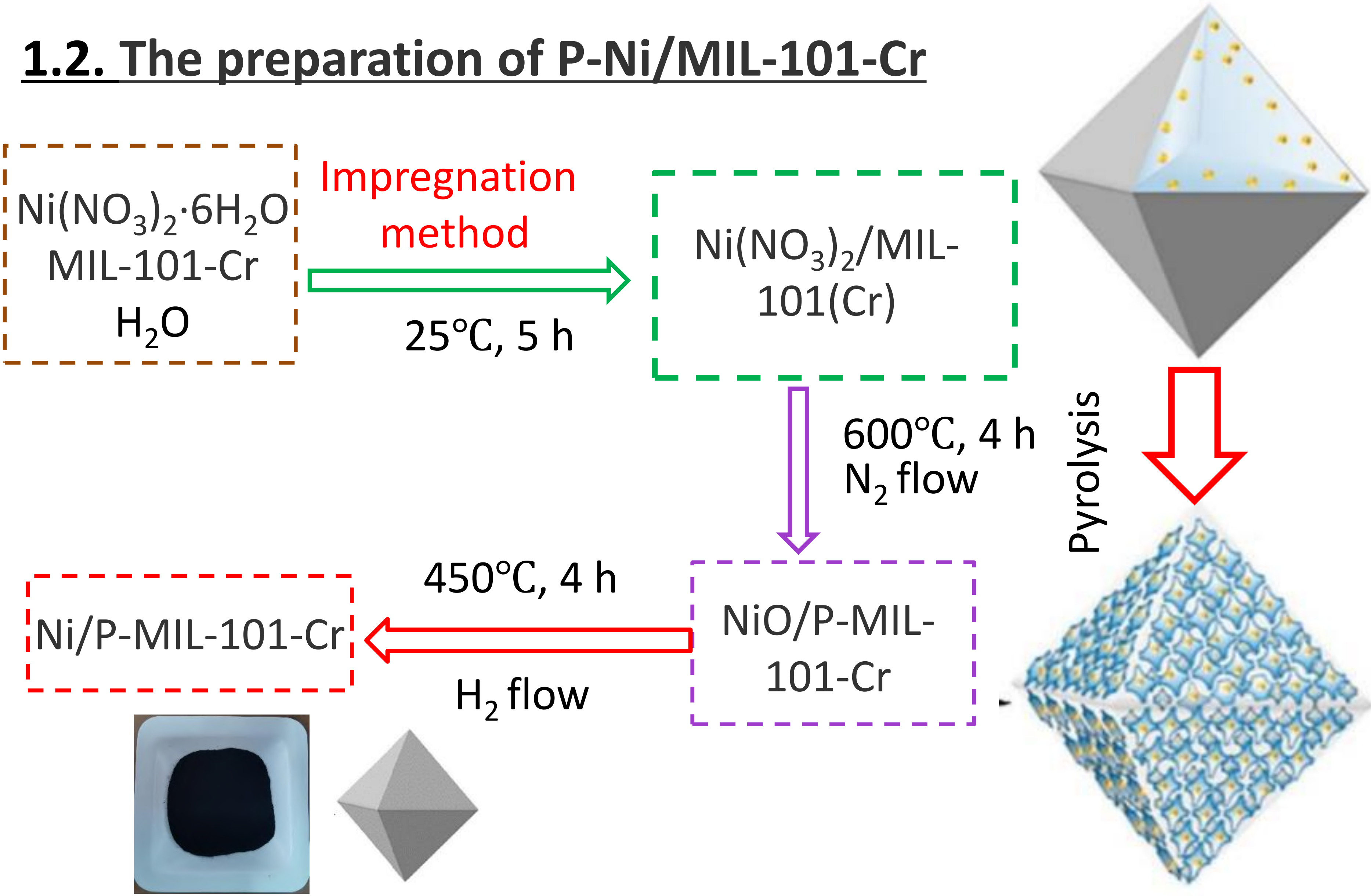



Fig. Schematic diagram of MIL-101 supported Ni to prepare P-Ni/MIL-101-Cr catalyst

# Methodology- Hydrodeoxygenation reaction

The HDO reaction was carried out in a 100 mL reactor.

⇩

10 g Feedstock + 0.5g catalyst at a mass ratio of 20:1 added into the reactor and sealed.

⇩

The reaction temperature is 400 ℃,purified $H_2$ pressure and the mixture stirred at 200 r/min for 3 h.

⇩

The obtained liquid and gas product are collected and analyzed using GC and GCMS.

⇩

The used catalyst is washed and kept for reusability studies with the same method and same parameters.

Product: Green Diesel (C15-C18)

# Catalyst surface and pore (BET)

| Samples | $S_{BET}(m^2/g)$ | Pore Volume($cm^3/g$) | Average pore size (nm) |
|---|---|---|---|
| **MIL-101-Cr** | 2923.73 | 1.52 | 2.09 |
| **P-MIL-101-Cr** | 277.13 | 0.21 | 5.37 |
| **P-4%Ni/MIL-101-Cr** | 230.21 | 0.19 | 4.96 |
| **P-8%Ni/MIL-101-Cr** | 211.37 | 0.17 | 4.79 |
| **P-14%Ni/MIL-101-Cr** | 80.50 | 0.13 | 4.20 |
| **P-25%Ni/MIL-101-Cr** | 52.87 | 0.07 | 4.09 |

<2.35nm

>2.35nm

**Table 3** $S_{BET}$, pore volumes, average pore sizes of the samples.

**Palmitic Acid's average molecular size is 2.35nm**

# Catalyst morphology images (HRTEM)

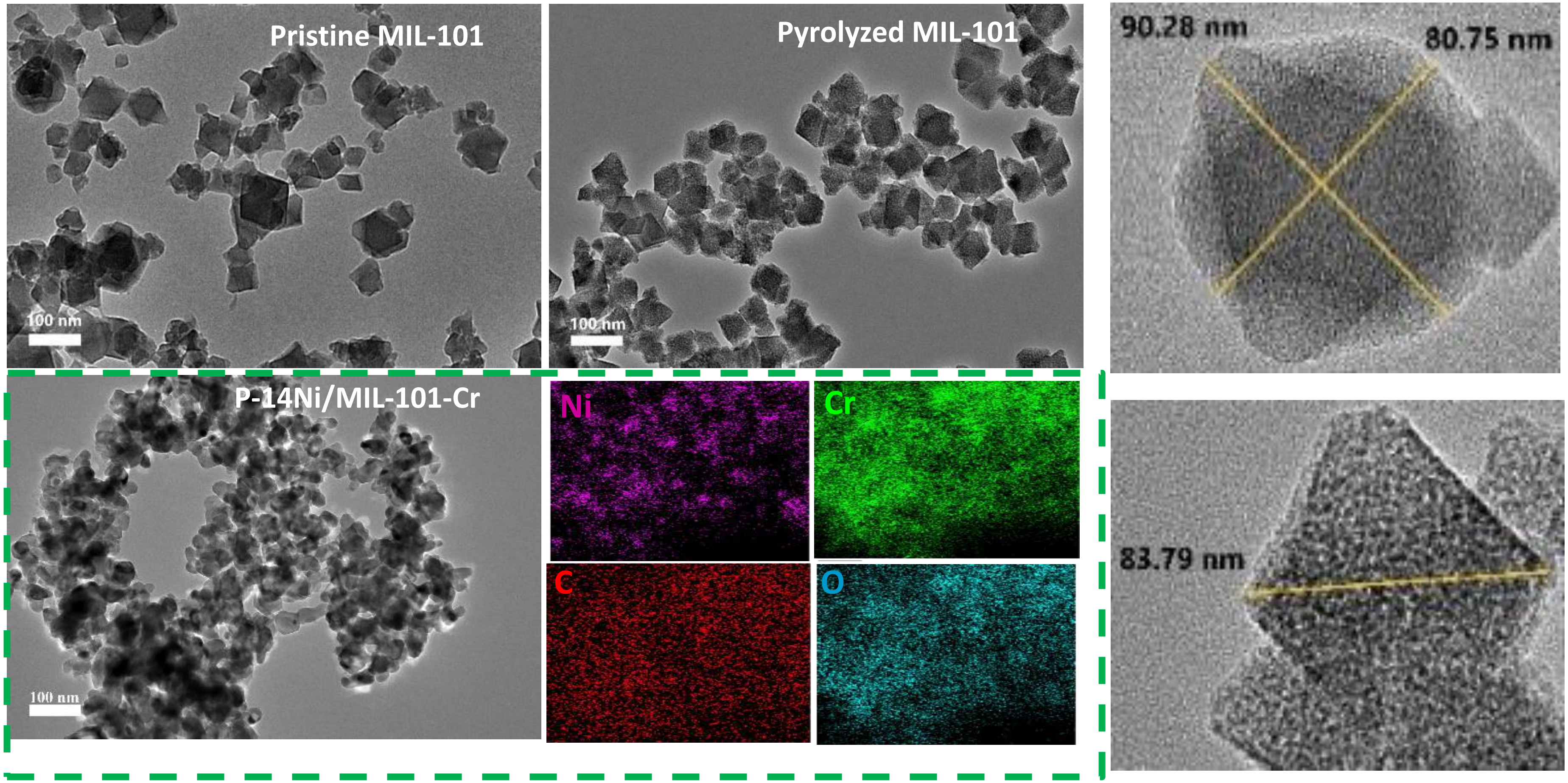



**Fig. HR-TEM images of catalyst**

- ✓ The elements distributed uniformly in the catalyst indicated that the crystal's internal structure did not collapse or aggregate.
- ✓ The octahedral structure of MIL-101-Cr is maintained after pyrolysis.

# Catalytic hydrodeoxygenation reaction of Palmitic acids

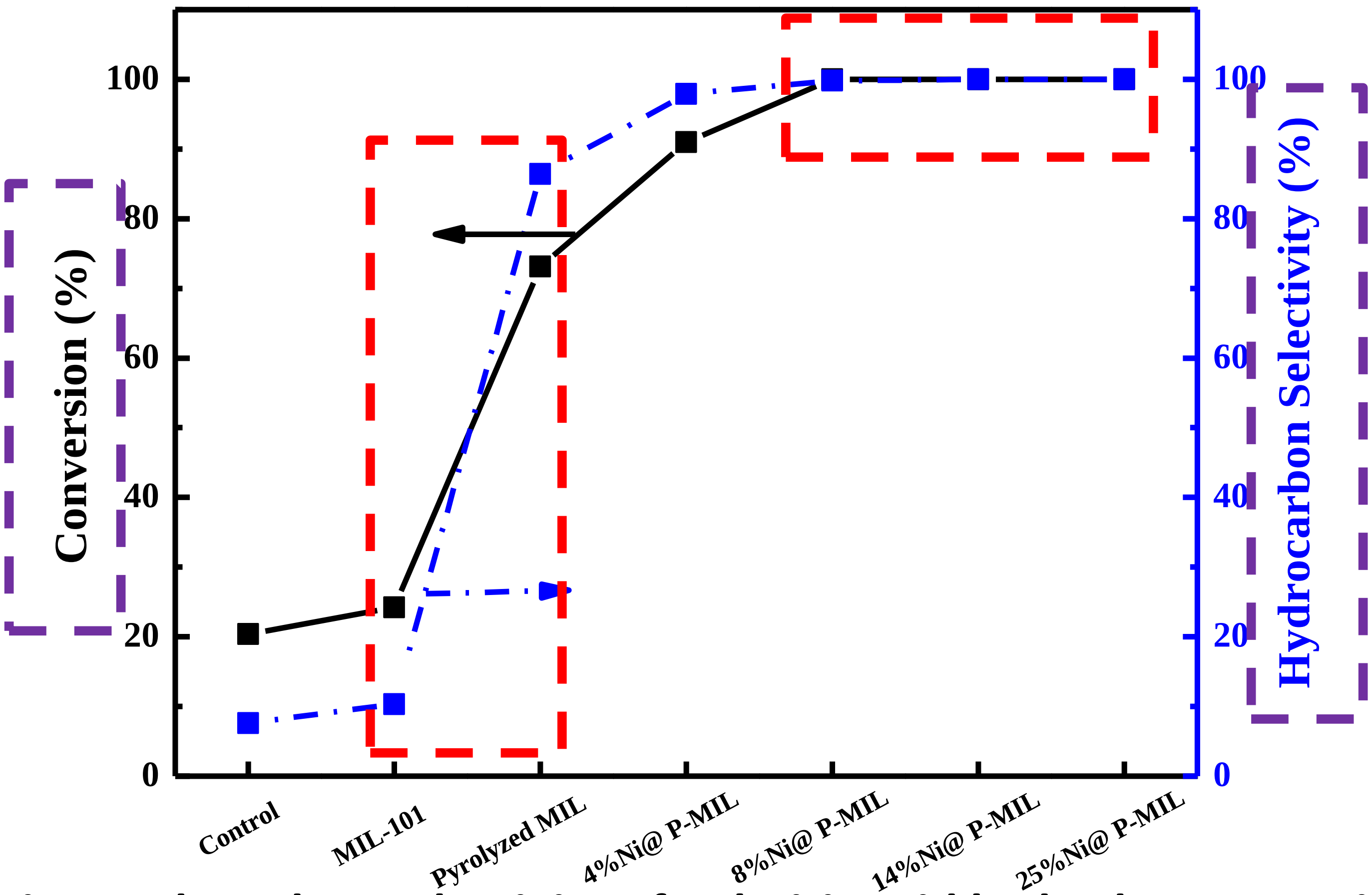



**Fig. Conversion and product selectivity of palmitic acid hydrodeoxygenation reaction using Ni/P-MIL-101 catalysts**

✓ Ni loading above 8% P-MIL-101 can show the best activity with 100% of conversion and 100% of hydrocarbon selectivity.

# Catalytic activity at different temperature

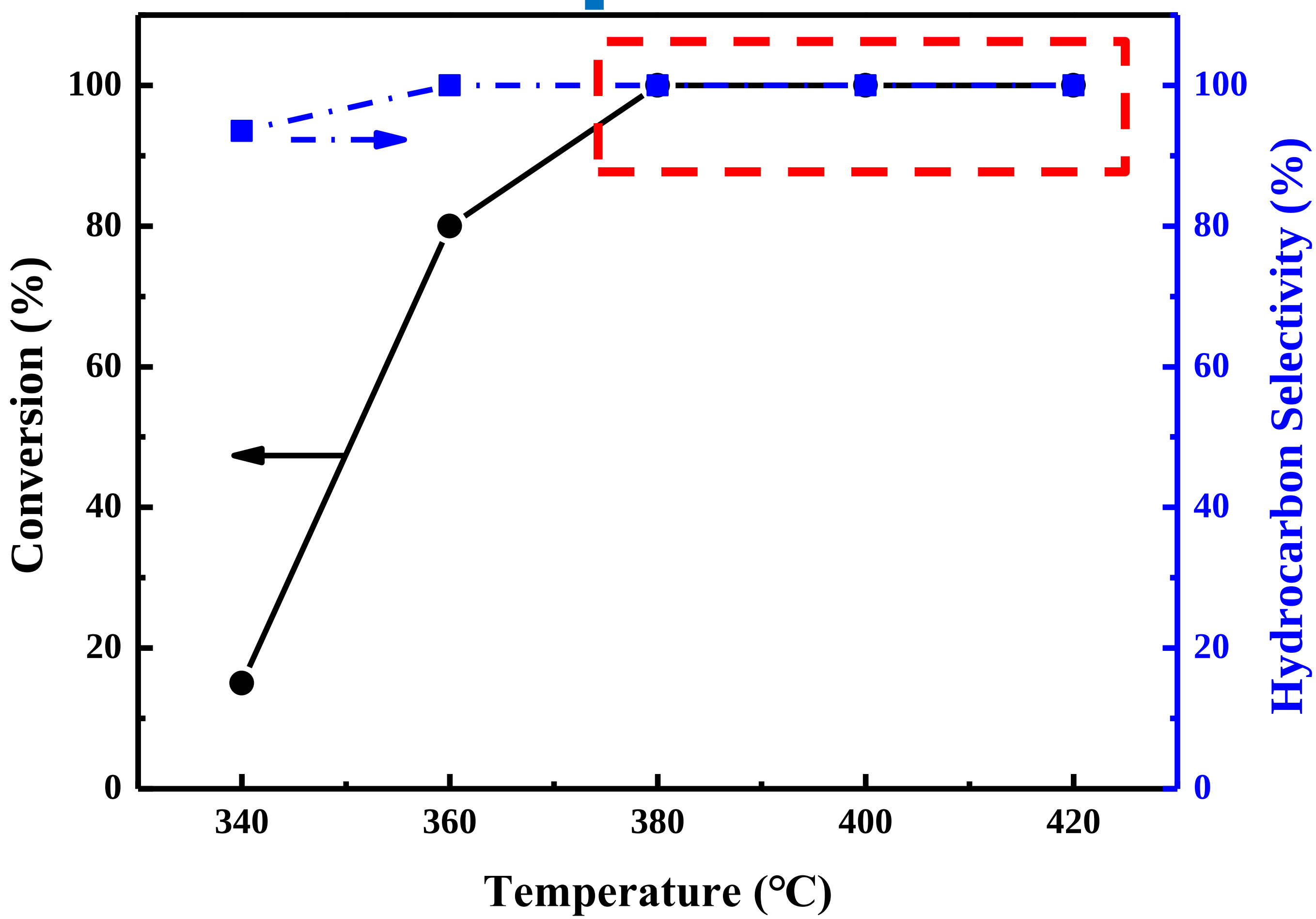



**Fig. Effect of temperature on catalytic palmitic acid hydrodeoxygenation reaction**

- ✓ Optimization reaction temperature is 400°C, which has 100% of conversion and selectivity and 91.1% of green diesel selectivity.

# Reusability studies of 8-25wt%Ni/P-MIL-101 catalysts

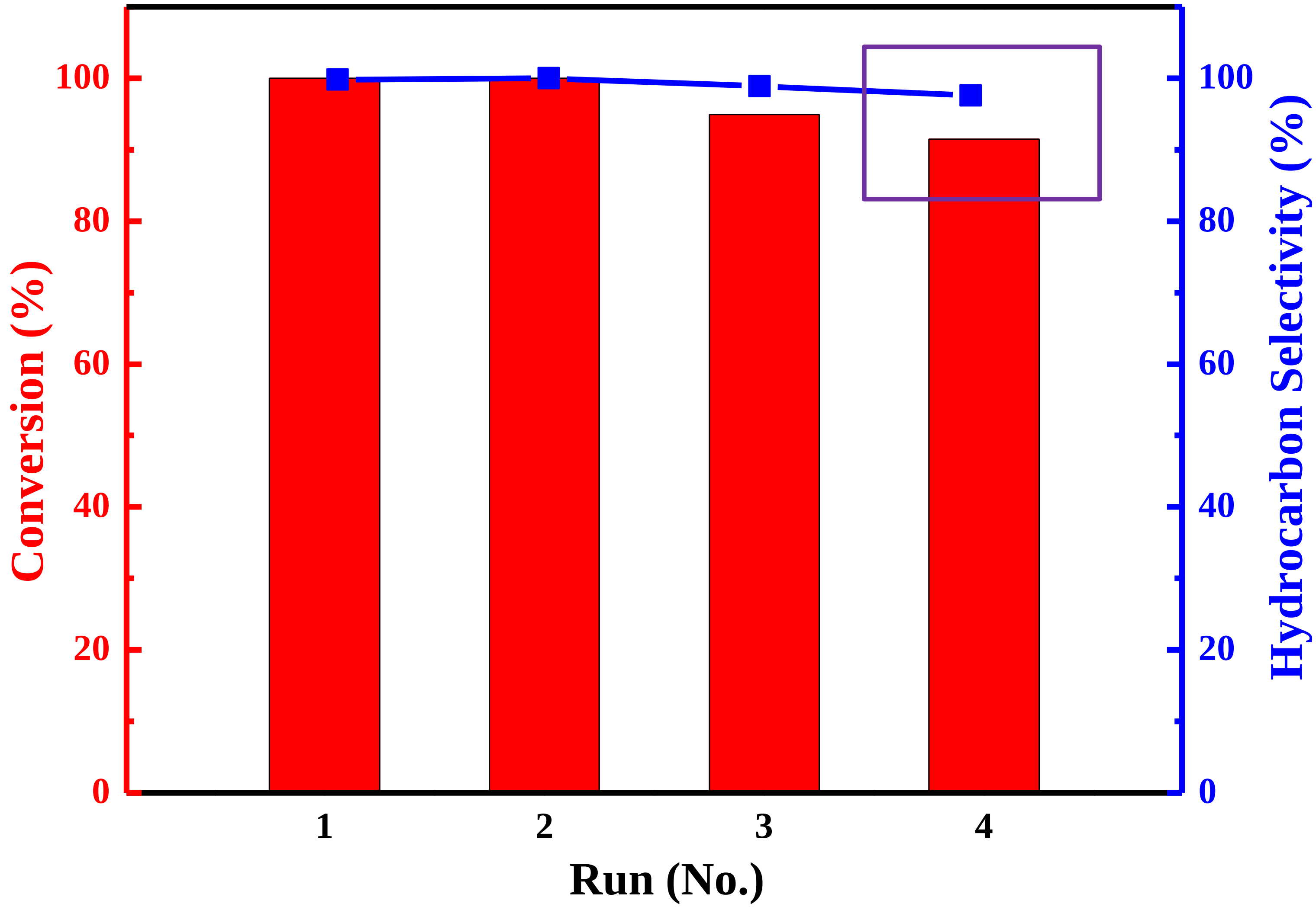



Fig. Catalytic HDO of Palmitic acid using 8%Ni/P-MIL-101-Cr catalyst

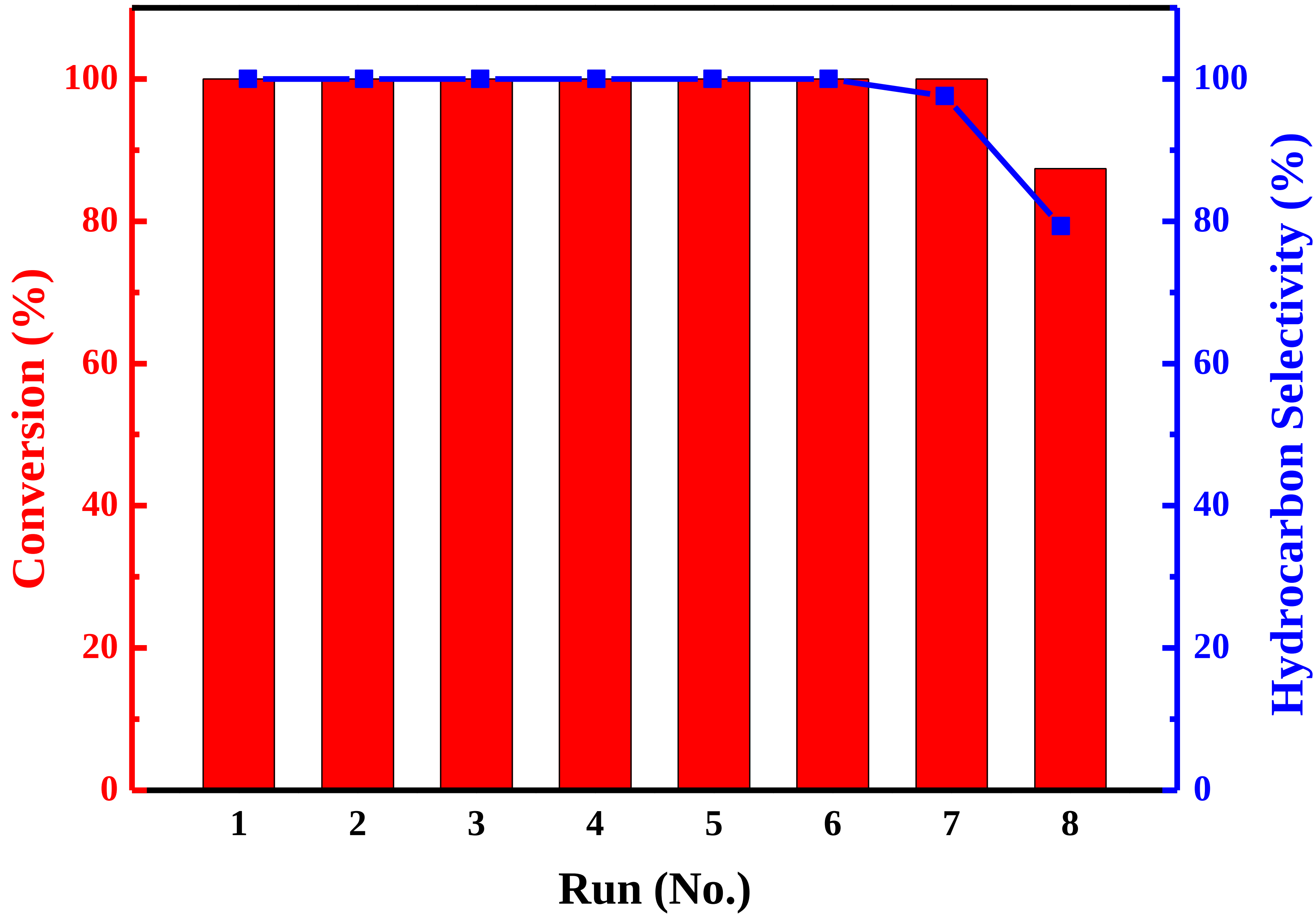



**Fig. Catalytic HDO of Palmitic acid using 25%Ni/P-MIL-101-Cr catalyst**

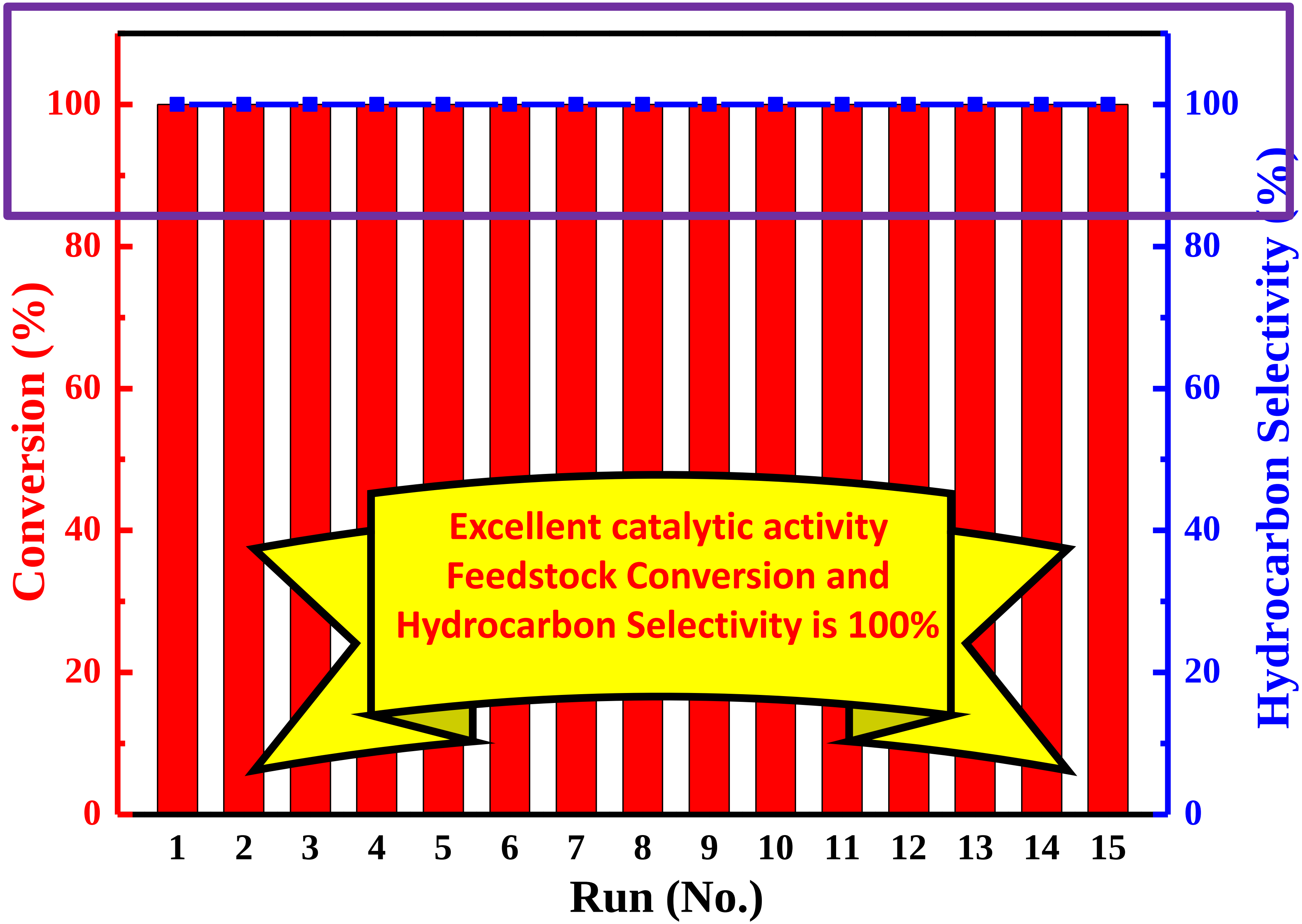



Fig. Catalytic HDO of Palmitic acid using 14%Ni/P-MIL-101-Cr catalyst

# Analysis of used catalysts - P-14%Ni/MIL-101

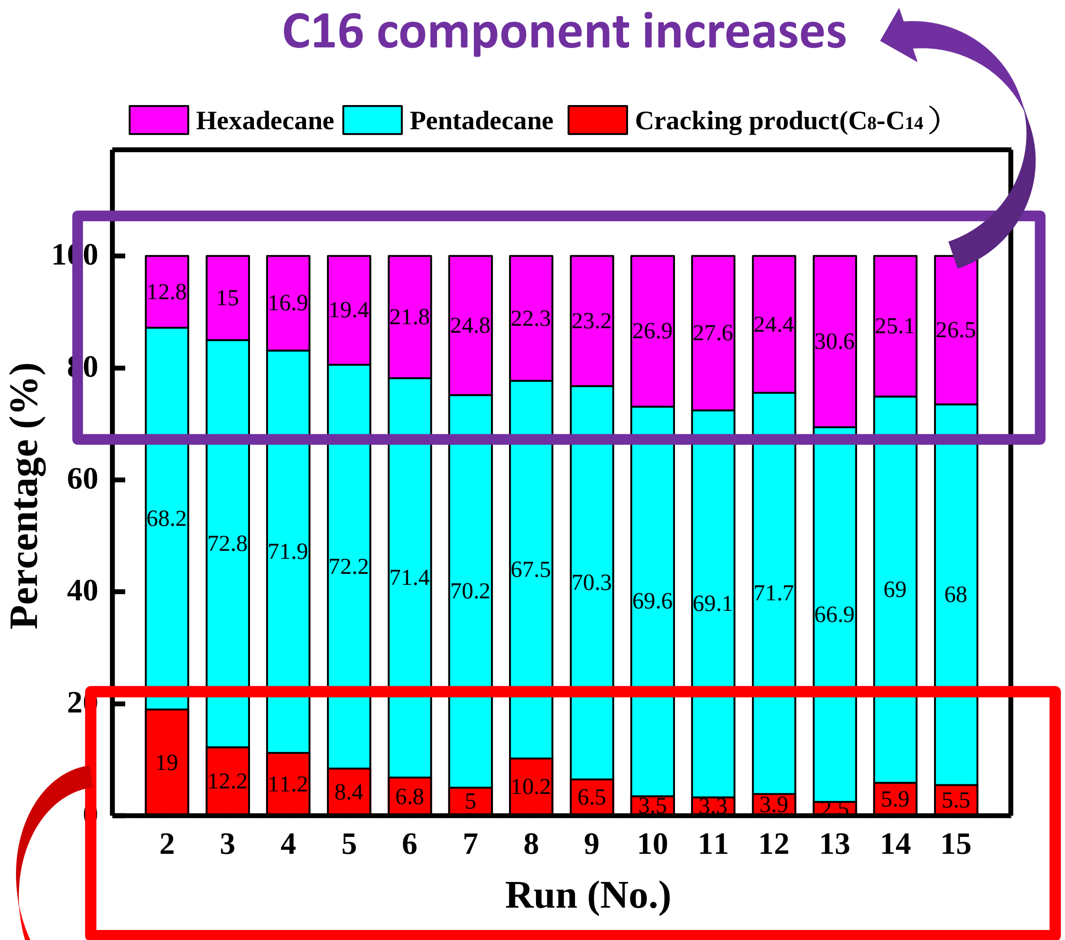



**Fig. Product distribution.**

•The cracking component decreases

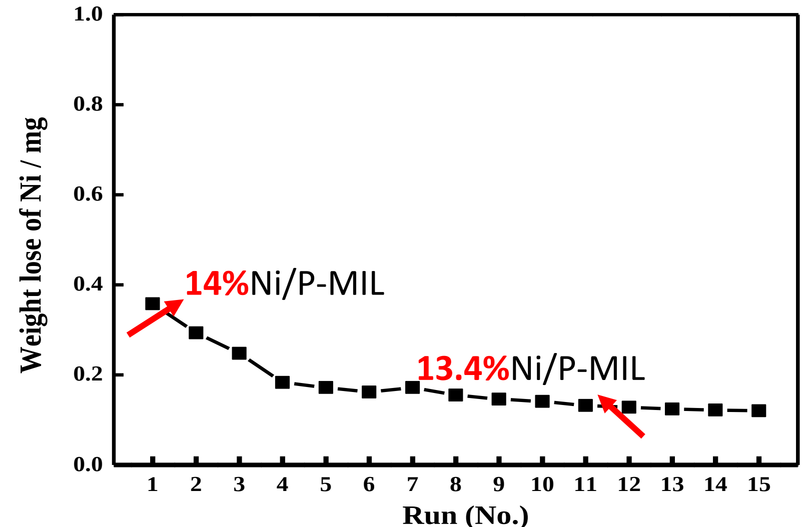



**Fig. Ni metal leaching by AAS**

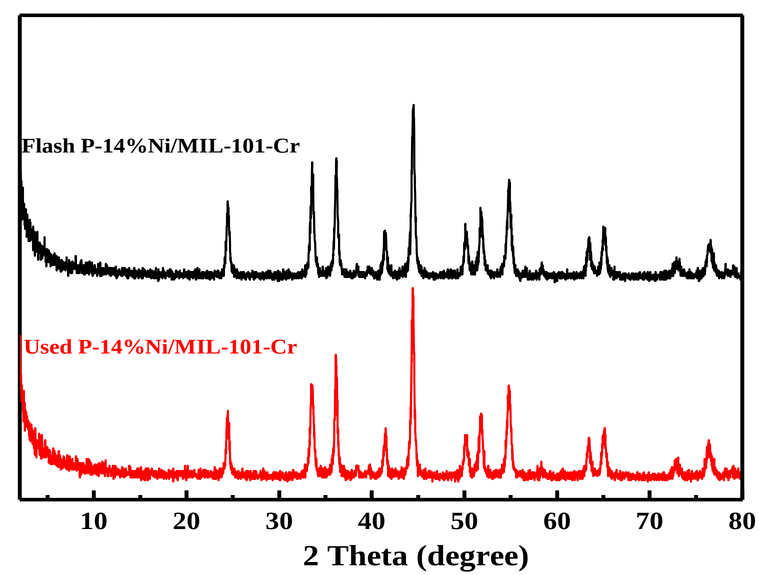



**Fig. XRD analysis for fresh and used catalyst**

- ✓ The Ni leaching is insignificant (AAS).
- ✓ The structure of the catalysts remained unchanged

# HDO with different feedstocks

| | Catalyst | Feedstock | Conditions | Catalyst loading (wt%) | Conversion (%) | Selectivity of paraffins (%) |
|---|---|---|---|---|---|---|
| **1** | 14 wt% Ni/P-MIL-101 | Palmitic acid | 3 h, 400 °C, 3MPa | 5 | 100 | 100 |
| **2** | 14 wt% Ni/P-MIL-101 | PFAD | 3 h, 400 °C, 3MPa | 5 | 99.7 | 100 |
| **3** | 14 wt% Ni/P-MIL-101 | Palm kernel oil | 3 h, 400 °C, 3MPa | 5 | 99.0 | 100 |
| **4** | 14 wt% Ni/P-MIL-101 | Waste cooking oil | 3 h, 400 °C, 3MPa | 5 | 97.1 | 100 |
| **5** | 14 wt% Ni/P-MIL-101 | Lauric acid | 3 h, 400 °C, 3MPa | 5 | 97 | 95.2 |
| **6** | 14 wt% Ni/P-MIL-101 | Fatty acid methyl easter (FAME) | 3 h, 400 °C, 3MPa | 5 | 100 | 100 |

**Table 4.** The catalytic effect of different feedstock in HDO

# Liquid product characterization

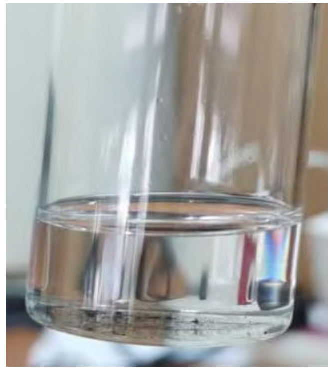
| No. | Fuel properties | Green fuel |
|---|---|---|
| 1 | Cloud Point (°C) | -21 |
| 2 | Flash Point (Pensky-Martens Closed Cup) | 132.7 |
| 3 | Kinematic Viscosity (100°C) (cSt) | 0.40 |
| 4 | Kinematic Viscosity (40°C) ( cSt) | 1.7 |
| 5 | Pour Point (°C) | -17 |
| 6 | Ash Content (wt%) | <0.01 |
| 7 | Carbon Residue (MCRT Method) (wt%) | 0.05 |
| 8 | Cetane Index (by Calculation) | 88.5 |
| 9 | Volatility Characteristic (Distillation)(°C) | 248 |
| 10 | Heating value, MJ/kg | 42 |


Average mass balance of Hydrodeoxygenation reaction

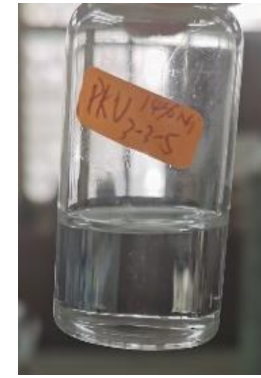
| Reaction | Feedstock | Liquid product | water | Char + residue |
|---|---|---|---|---|
| | (g) | (g) | (g) | (g) |
| 1 | 10.03 | 7.63 | 1.12 | 0 |
| 2 | 10.01 | 7.81 | 1.24 | 0 |
| 3 | 10.01 | 7.54 | 1.16 | 0 |
| Average | 10.02 | 7.66 | 1.17 | 0 |

Green Diesel produced from PFAD

# Feedstocks and Products after HDO

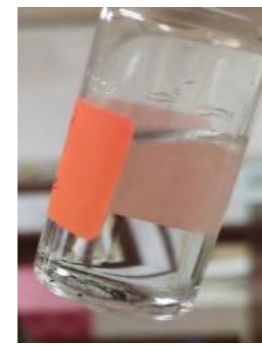



Palmitic acid

Palm kernel oil


Lauric acid

Waste cooking oil

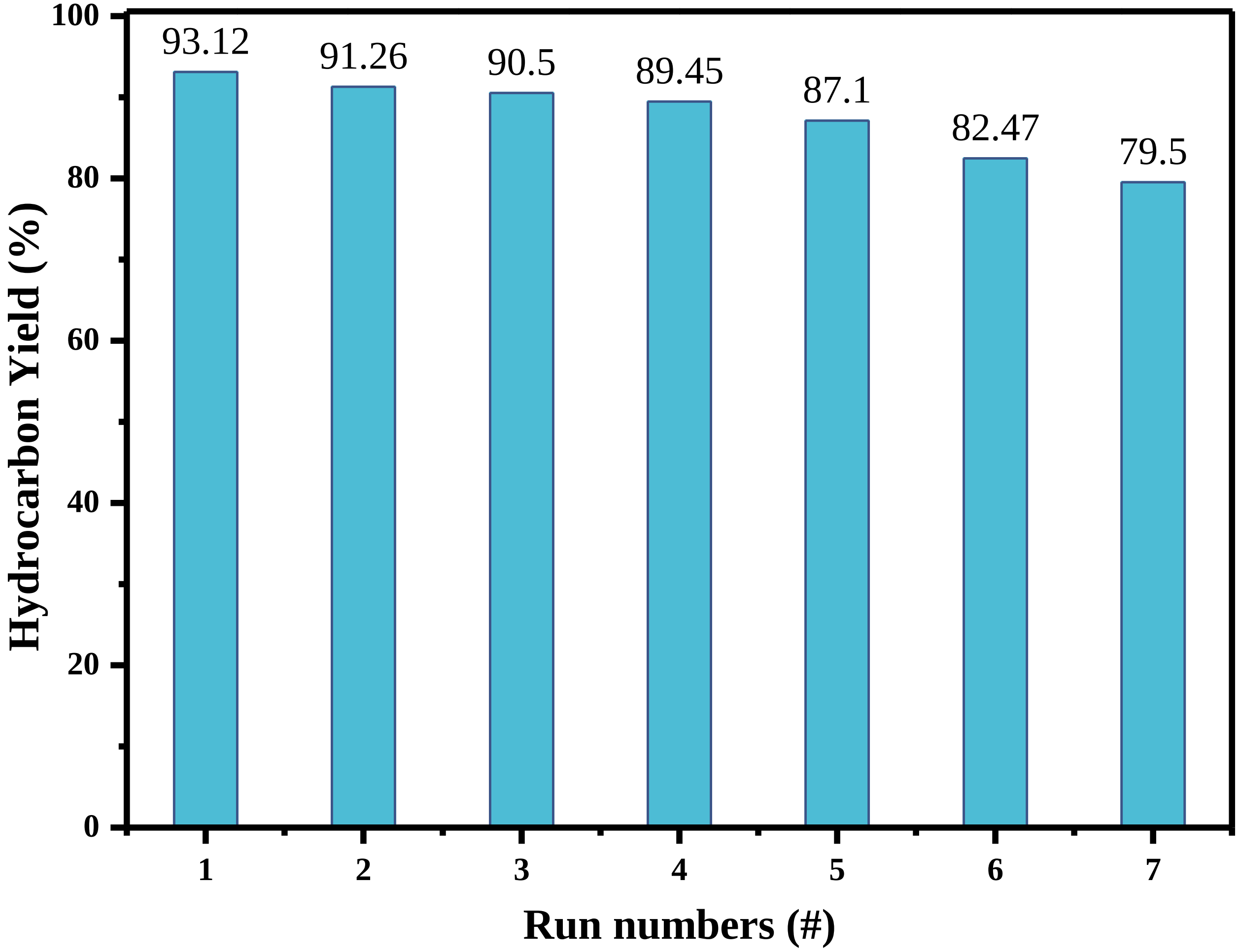
PFAD (SOPB Sample)

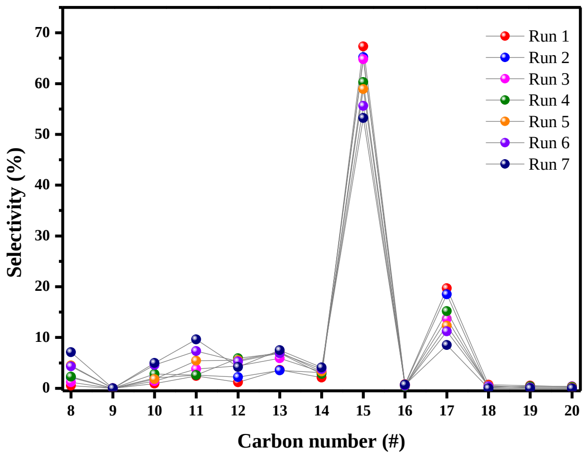

FAME

# Literatures comparison of our innovation

| | Catalyst | Feedstock | Conditions | Solvent | Catalyst loading (wt%) | Conversion (%) | Selectivity (%) | Reusability | Ref |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 10 wt% La/HZSM5 | Oleic acid | 2 h, 400 °C, 5MPa | Free | 5 | 100 | 97 | 4 | Azreena, et, al, 2022 |
| **2** | $MoO_2$/CNTs | Palmitic acid | 4 h, 220 °C, 4MPa | Decane | 50 | 100 | 92.2 | 5 | Ranran et, al, 2015 |
| **3** | 7 wt% Ni/RM | Palmitic acid | 4 h, 300 °C, 4MPa | Decane | 20 | 100 | 100 | 3 | Jin et, al, 2022 |
| **4** | 20%Ni/$MoO_2$@$Mo_2CT_x$ | Palmitic acid | 4 h, 280 °C, 4MPa | Decane | 20 | 100 | 97 | 5 | Liang et, al, 2020 |
| **5** | Pt/$H_3PO_4$@MIL-101(Cr) | Oleic acid | 2 h, 300 °C, 2MPa | Decane | 20 | 95 | 75.5 | -- | Dieu-Phuong et, al, 2020 |
| **6** | 8%NiO/$NbOPO_4$ | Palm oil | 5 h, 250 °C, 3.5MPa | Free | -- | 85.7 | 97.1 | -- | Mustika et, al, 2020 |
| **7** | 25 wt% Ni/P-MIL-101 | Palmitic acid | 3 h, 400 °C, 3MPa | Free | 5 | 100 | 100 | 8 | This work |
| **8** | 14 wt% Ni/P-MIL-101 | Palmitic acid | 3 h, 400 °C, 3MPa | Free | 5 | 100 | 100 | 15 | This work |

# Deoxygenation of PFAD




Feedstock: **PFAD**

Catalyst: 14wt% Ni/P-MIL-101
Reaction temperature: 320℃
Reaction time: 3h
Catalyst loading: 3wt%
Condition: $N_2$

# Publications

| NO | TITLE | JOURNAL | STATUS |
|---|---|---|---|
| **1** | Catalytic ketonization of palmitic acid over a series of transition metal oxides supported on zirconia oxide-based catalysts. | RSC Advances | Published (2021) |
| **2** | Development of Porous MIL-101 Derived Catalyst Application for Green Diesel Production. | Fuel | Accepted (2023) |
| **3** | A method of Using A Heterogenous Catalyst for Preparing Green Diesel Via Hydrodeoxygenation (HDO) reaction of Fatty acids feedstock. | Patent Pending (Malaysia) | PI2022007531 (2022) |

# Conclusions


- PFAD as feedstock has great potential to be to used produce value added chemicals such as bio-lubricants and biofuels. (Green diesel and Sustainable Aviation Fuel (SAF))

- Advancement in catalyst technology makes this conversion process more feasible and economical.

“A man must never forget that fossil fuels are very precious and biofuels are the wisest choice”

**SOP EDIBLE OILS SDN. BHD.** (538248-X)
(A SUBSIDIARY OF SARAWAK OIL PALMS BERHAD)

12 March 2021

The Senior Lecturer
Department of Science and Technology
Faculty of Humanities, Management and Science,
Universiti Putra Malaysia Kampus Bintulu,
97008 Bintulu, Sarawak,
Malaysia

Attn: Dr Sivasangar Seenivasagam

Dear Dr,

**RE: Palm Free Acid Distillate Samples**

Your email requisition on Palm Fatty Acid Distillate ("PFAD") to our Mill Controller Mr Thong Kuok Ling dated 25 February 2021 is refers.

We hereby provide our PFAD samples as per requested as part of our support/contribution to your research project on conversion of PFAD into diesel range hydrocarbons.

2. We also acknowledged that this research proposal is currently under the evaluation and it may eligible to get funding from Ministry of Education under FRGS grant scheme.

3. Last but not least, we are glad to participate in this research project which benefits for the Oil Palm Industry. Please do not hesitate to contact us if you need any further assistance.

Yours faithfully,

Kiu Kwong Chiang
Controller (Operations)

No. 124-126, Jalan Bendahara, P. O. Box 547, 98007 Miri, Sarawak, Malaysia.
Tel: 085-436969 Fax: 085-432929 E-mail: info@sop.com.my

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**IAN 言创**
Intellectual Property

Our Ref : IAN/PT/2022/049
Date : 21.12.2022

University Putra Malaysia — By email
43400,UPM Serdang,
Malaysia

Attn: Dr. Sivasangar,

**Re: Patent Application for Method For Using A Heterogenous Catalyst For Preparing Green Diesel By Using Hydrodeoxygenation (HDO) Reaction of Fatty Acids Feedstock**

We refer to the above matter.

1. Kindly find attached herewith the following documents for your kind perusal: -

(a) [Final] Patent Specification (Word File); and
(b) [Final] Patent Drawing (PDF File).

2. If the patent specification and drawings are acceptable for us to proceed with filling of the patent application in Malaysia, kindly confirm your decision by executing the Patent Confirmation Sheet in page 2 of this letter and return to us the duplicate copy of this letter for our record and further action before or by **23.12.2022.**

Thank you.

Yours sincerely,

**Ian Intellectual Property Sdn. Bhd.**

**IAN INTELLECTUAL PROPERTY SDN. BHD.** (1173398-T)
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# Research Team

**Dr Sivasangar Seenivasagam**
**(PutraCAT, UPM)**
**Project Leader**

Prof Datuk Dr Taufiq Yap Yun Hin
(PutraCAT, UPM)

Dr Mohd Lokman Ibrahim
(UITM)

Dr Lee Hwei Voon
(Nanocat, UM)

# Catalyst composition (XRF& ICPOES)

| Catalysts | Elements surface analysis (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Theoretical | XRF | ICPOES | EDX | | | |
| | Ni | | | C | O | Cr | Ni |
| **MIL-101-Cr** | -- | -- | -- | 41.1 | 38.2 | 20.7 | -- |
| **P-MIL-101-Cr** | -- | -- | -- | 54.3 | 17.5 | 28.2 | -- |
| **P-4%Ni/MIL-101-Cr** | 5 | 4.5 | 4.3 | 50.7 | 19.1 | 27.9 | 2.3 |
| **P-8%Ni/MIL-101-Cr** | 10 | 8.6 | 8.4 | 46.1 | 20.8 | 27.3 | 5.8 |
| **P-14%Ni/MIL-101-Cr** | 15 | 14.3 | 14.1 | 47.3 | 16.5 | 25.9 | 10.3 |
| **P-25%Ni/MIL-101-Cr** | 25 | 26.1 | 25.8 | 45.8 | 14.3 | 23.5 | 16.4 |

**Table 2** Elemental composition of the catalysts.

✓ The content of added elements (dopants) in MIL-101-Cr based catalyst are consistent with the theoretical values.

# Physicochemical properties(XRD)

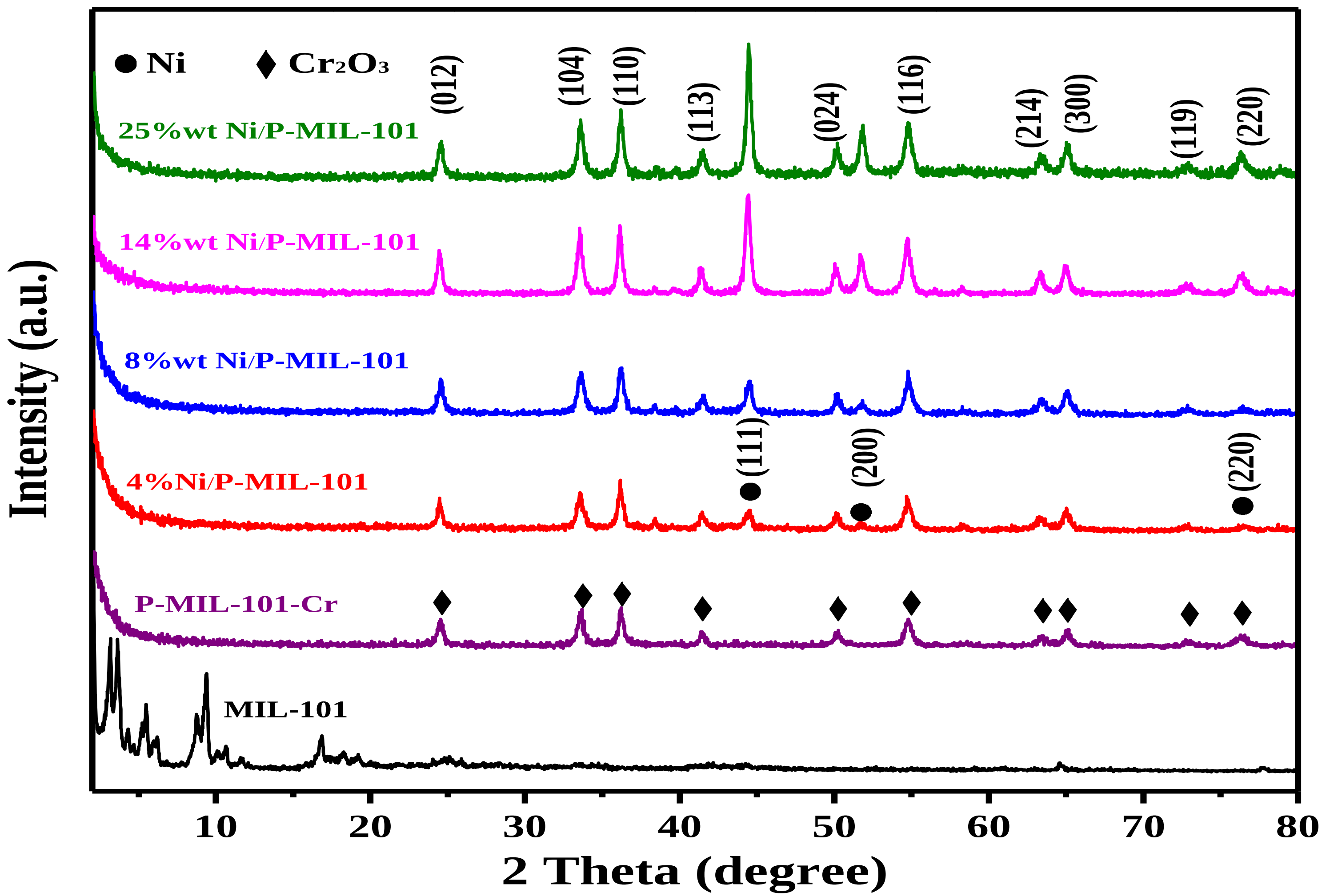



**Fig.8. X-ray diffractograms of the catalysts .**

✓The catalyst shows the presence of $Cr_2O_3$ and Ni metal.

# Catalyst composition (FTIR)

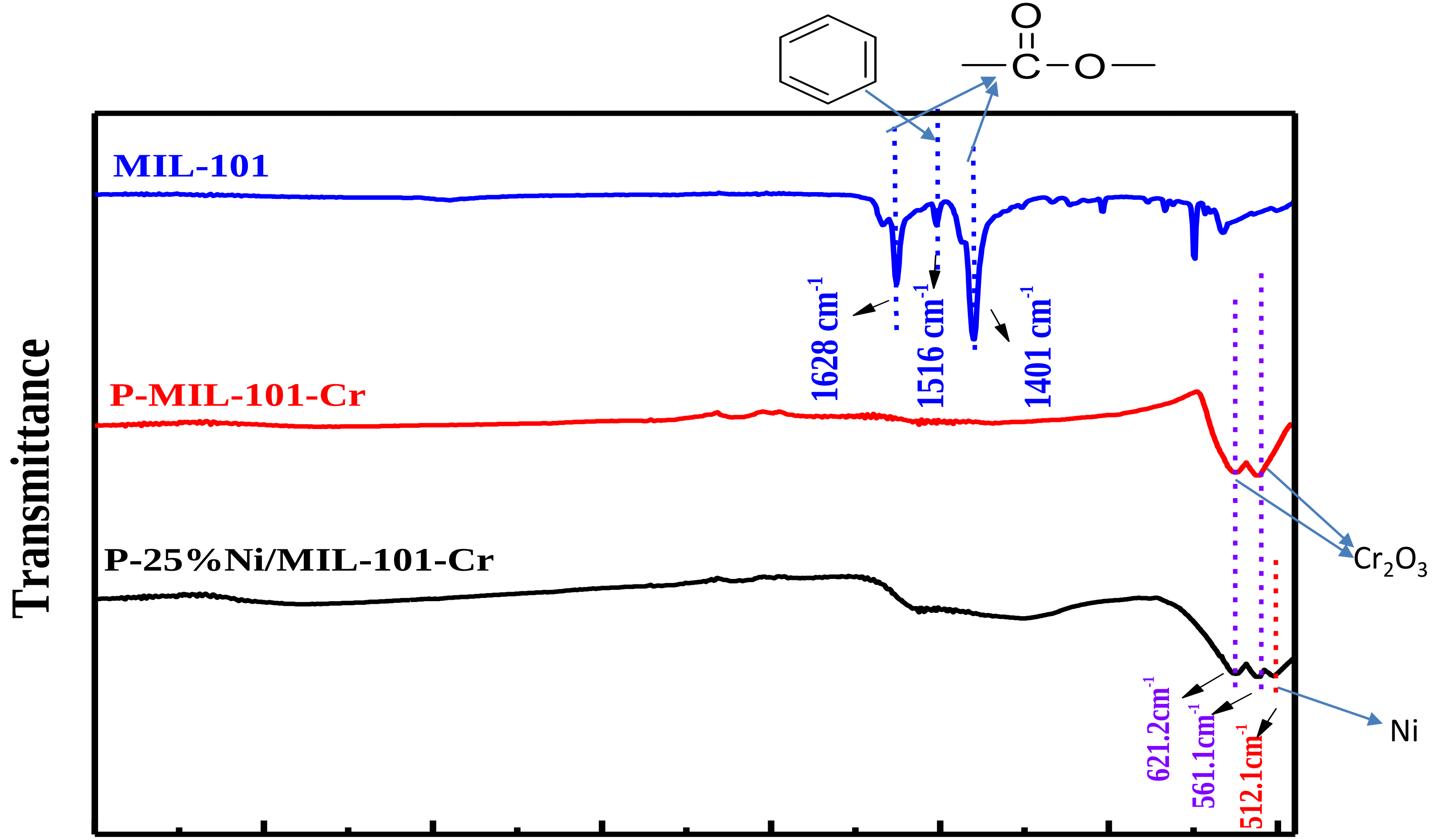



**Fig.9. FTIR spectrum of the catalysts**

✓ Addition of Ni did not alter the presence $Cr_2O_3$ peaks and a new peak correspond to Ni appears in the spectrum

# Analysis of used catalysts - 25%Ni/P-MIL-101

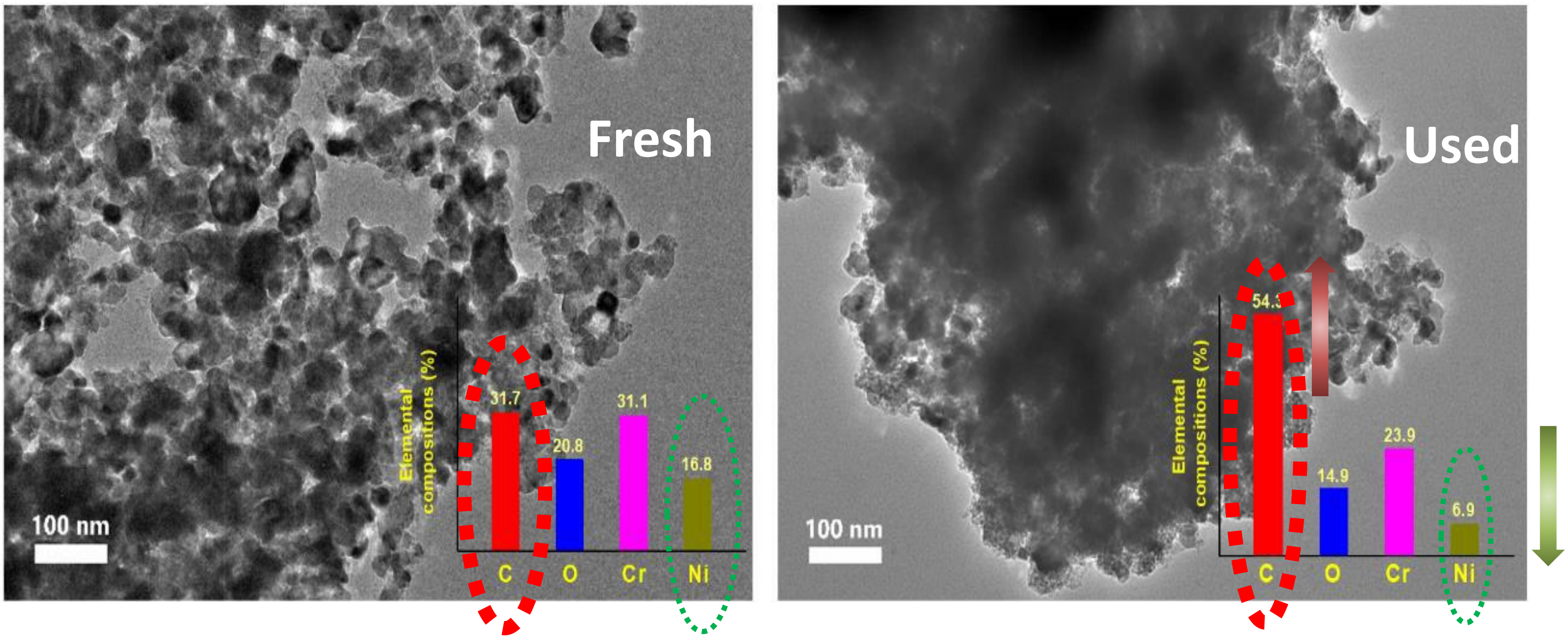



Fig. HRTEM-EDX analysis for fresh and used P-25Ni%-MIL-101 after 8th runs.

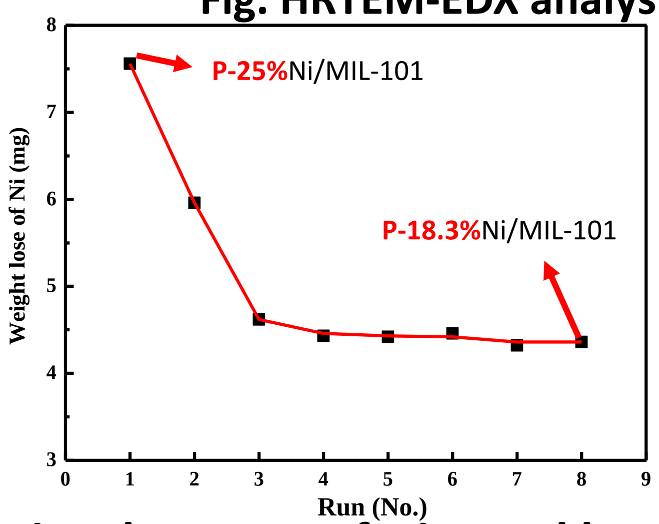



Fig. The curve of Ni metal leaching

**The Ni loading is too high and Ni composition started drop from 25% to 18.3%.**

# Catalyst composition and thermal properties

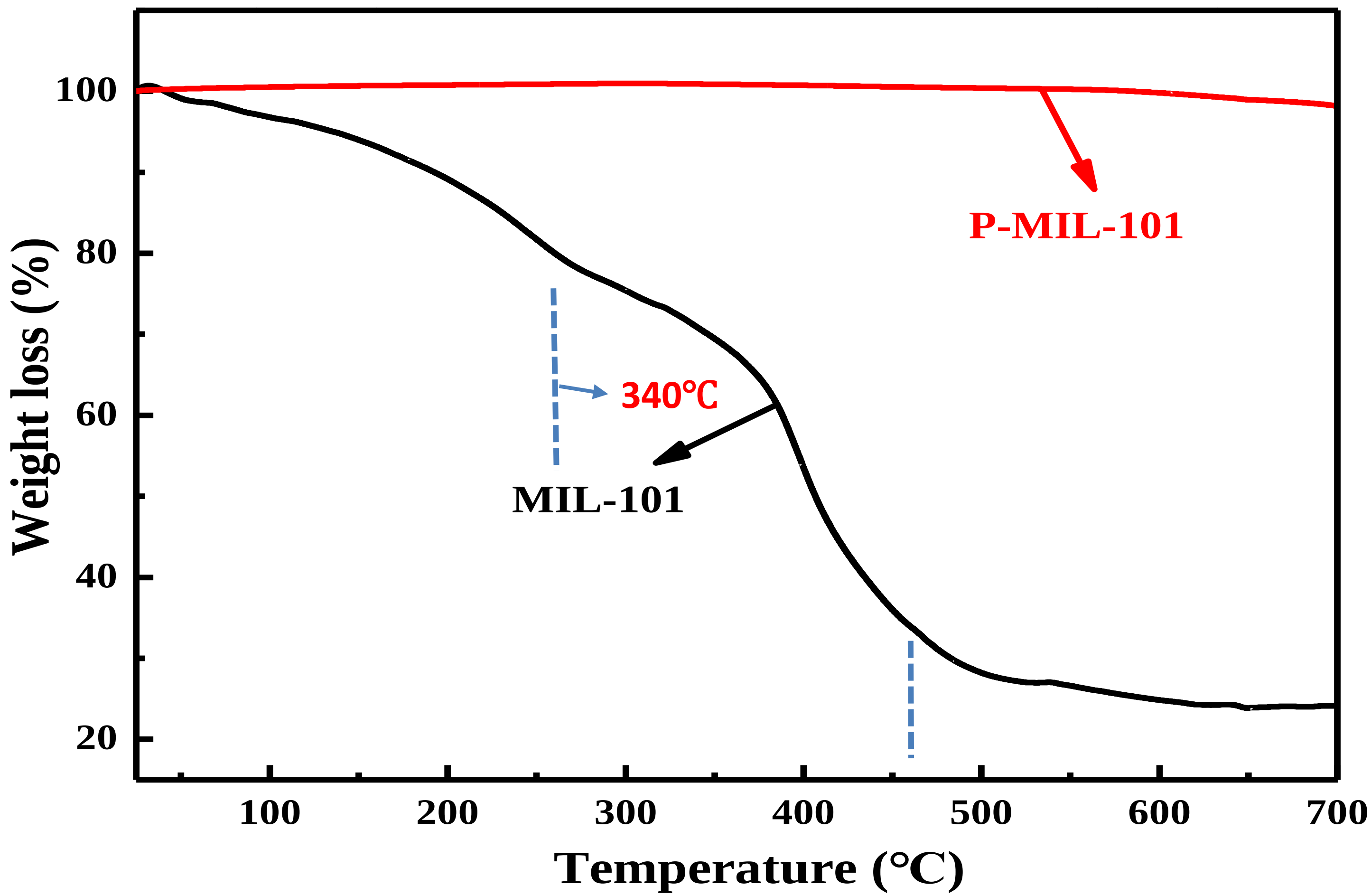



**Fig . Thermal stability of pristine and pyrolyzed MIL-101.**

✓ The weight of catalyst after pyrolysis didn't change prior to 500℃，so it can satisfy the experiment's requirements.

# Hydrocarbon Product Quality

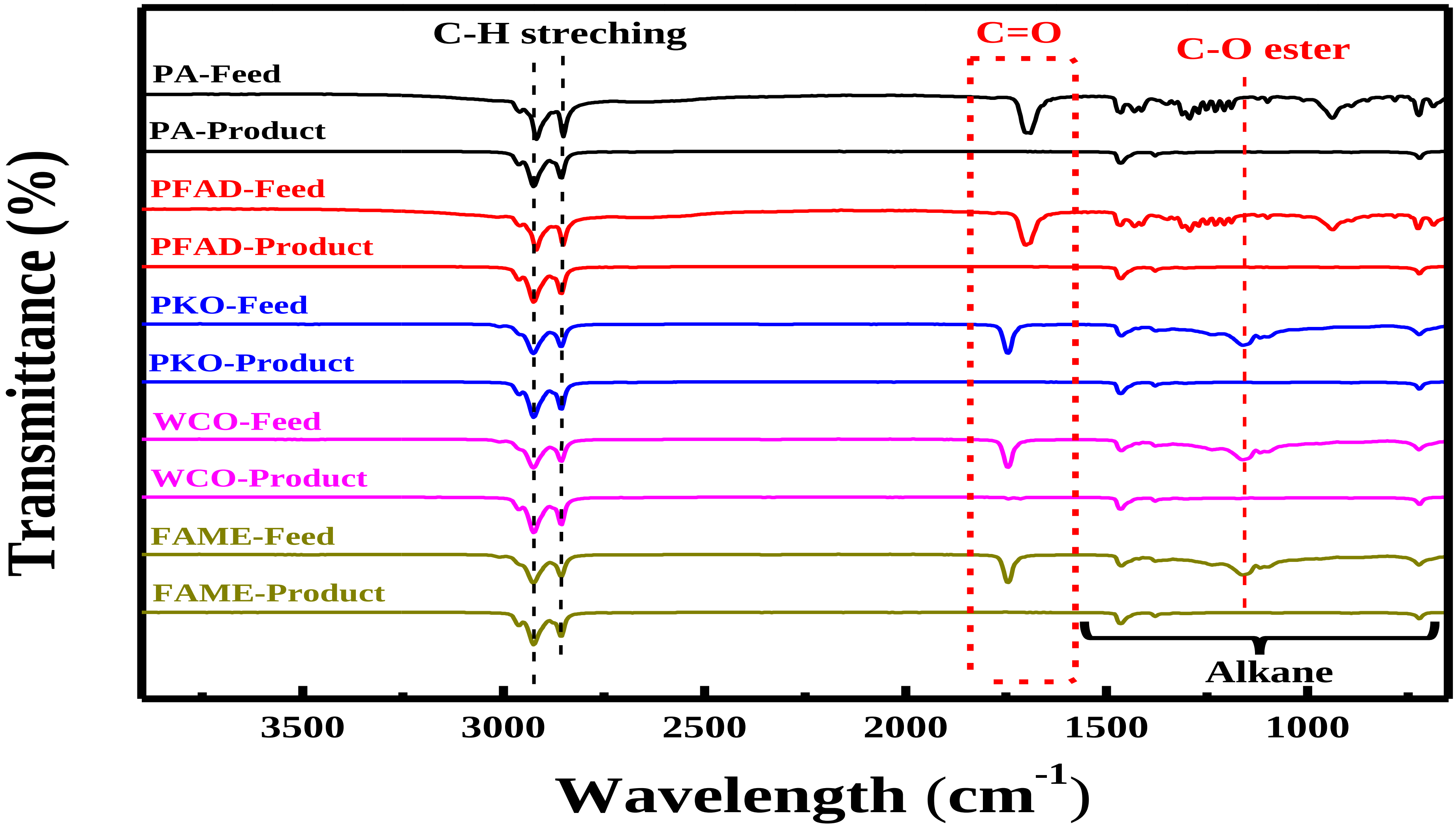



**Fig. FTIR spectrum of the feedstocks and their products**

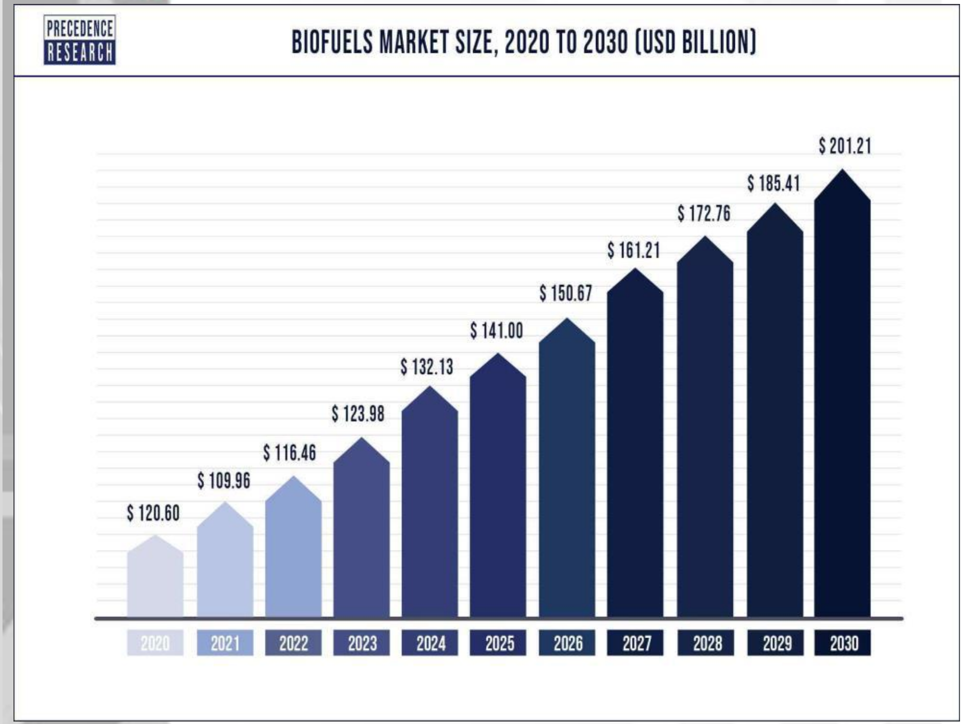
✓ All oxygen-containing functional groups were removed.

# HDO Reaction Mechanism

## Possible reaction paths of hydrodeoxygenation

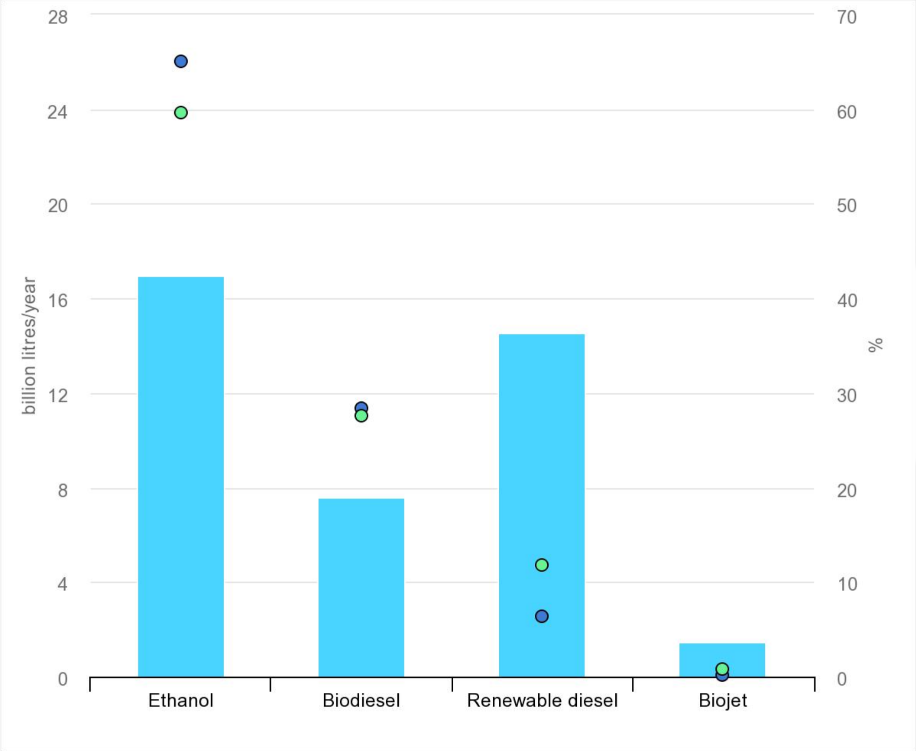

Fig. Possible reaction paths of hydrodeoxygenation (HDO).

# Global Biofuel Market Analysis




Biofuels Market Share, By Fuel Type, 2020

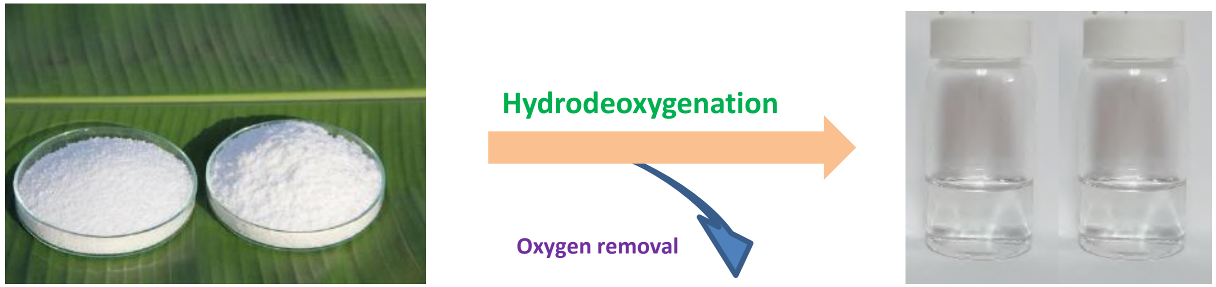
| Fuel Type | 2020 (%) |
|---|---|
| Biodiesel | 28.7% |
| Ethanol | 71.3% |




IEA, Biofuel demand growth and share of total demand by fuel, 2021-2026, IEA, Paris https://www.iea.org/data-and-statistics/charts/biofuel-demand-growth-and-share-of-total-demand-by-fuel-2021-2026.

With Knowledge We Serve

# Optimization deoxygenation study




Palmitic acid → Green diesel

**Table 5.** The catalytic effect of different reaction conditions in HDO

| | Catalyst | Feedstock | Conditions | Catalyst loading (wt%) | Conversion (%) | Selectivity of paraffins (%) |
|---|---|---|---|---|---|---|
| 1 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 3 h, 400 °C, 3MPa $H_2$ | 5 | 100 | 100 |
| 2 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 2 h, 400 °C, 3MPa $H_2$ | 5 | 100 | 100 |
| 3 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 1 h, 400 °C, 3MPa $H_2$ | 5 | 100 | 100 |
| 4 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 2 h, 400 °C, 2MPa $H_2$ | 5 | 100 | 99.7 |
| 5 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 2 h, 400 °C, 1MPa $H_2$ | 5 | 100 | 100 |
| 6 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 2 h, 400 °C, 1MPa $H_2$ | 3 | 100 | 100 |
| 7 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 1 h, 400 °C, 1MPa $H_2$ | 3 | 99.7 | 99.7 |
| 8 | 14 wt% Ni/P-MIL-101 | Palmitic acid | 3 h, 350°C, $N_2$ | 3 | 96.5 | 95.7 |

Different time (entries 1–4)

# Commercial Technologies, Plants and Key Players

| Company | Product | Production capacity / Year (Million tons) | Technology/Process | Plant location |
|---|---|---|---|---|
| REG | Renewable diesel | 0.2 | Bio-Synfining | USA |
| eni | Green diesel | 0.5 to 1 | Ecofining™ process | Italy |
| DIAMOND GREEN DIESEL | Renewable diesel | 0.4 | Ecofining™ process | USA |
| UPM | BioVerno renewable diesel | 0.1 | HydroFlex™ | Finland |
| preem | Preem evolution diesel | Unknown | HydroFlex™ | Sweden |
| CETANE | Renewable diesel | Unknown | Hydrotreating | USA |
| NESTE | Neste MY renewable diesel | 2.6 | NEXBTL process | Finland, Holland, Singapore |
| TOTAL | Renewable diesel | 0.5 | Vegan® technology by Axens | France |
| AltAir Fuels | Renewable jet fuel | 0.15 | UOP Renewable Jet Fuel Process | USA |
| PETRIXO OIL & GAS | Renewable jet fuel | 0.5 | UOP Renewable Jet Fuel Process | UAE |

Currently, over 5.5 billion liters of renewable diesel is produced globally and is forecasted to grow up to 13 billion liters in 2024