

# Biojet fuel production from ring opening of biomass-derived aromatic hydrocarbons

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# Introduction

- **Petroleum Jet fuels consists primarily of hydrocarbon compounds: paraffins, cycloparaffins(naphthenes), aromatics, and olefins. The predominant classes of compounds are shown in the table below**

| <b>Compounds</b>           | <b>Composition (%)</b> |
|----------------------------|------------------------|
| N-alkanes                  | 43.81                  |
| Monosubstituted alkanes    | 27.72                  |
| Disubstituted alkanes      | 4.00                   |
| <b>Cyclohexanes</b>        | <b>4.30</b>            |
| Monosubstituted aromatics  | 3.41                   |
| Disubstituted aromatics    | 6.23                   |
| Multisubstituted aromatics | 5.65                   |
| Total                      | 95.12                  |
| *source: Air Force 1988    |                        |

# Introduction

- Bioderived jet fuels are produced from plant lipids, waste cooking oils or algae lipids
- The main characteristics of these bioresources are that they are long chain alkanes
- Lignocellulosic fuels derived from hydrotreating biomass pyrolysis oils are mostly cycloalkanes (naphthenes) which can only be used as blend stocks.

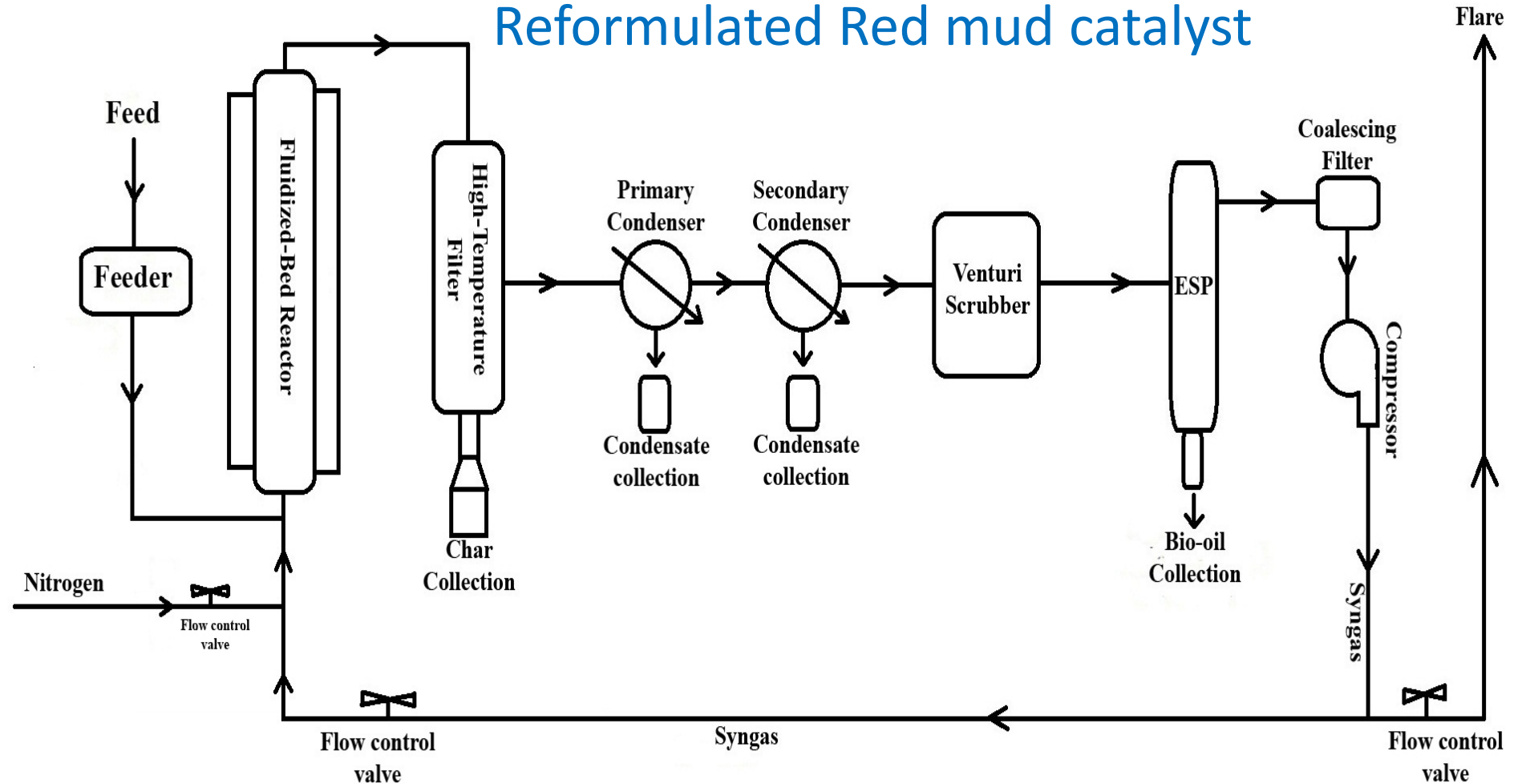
# Introduction

- **Objectives**

- Produce catalytic pyrolysis oils from lignocellulosic biomass feedstocks
- Develop catalyst to open the lignin aromatics rings and form long chain alkanes
- Hydrotreat pyrolysis oils with catalyst to produce alkanes, isoalkanes, cycloalkanes, and aromatics in one-step process that will qualify as jet fuel.

# Pyrolysis process

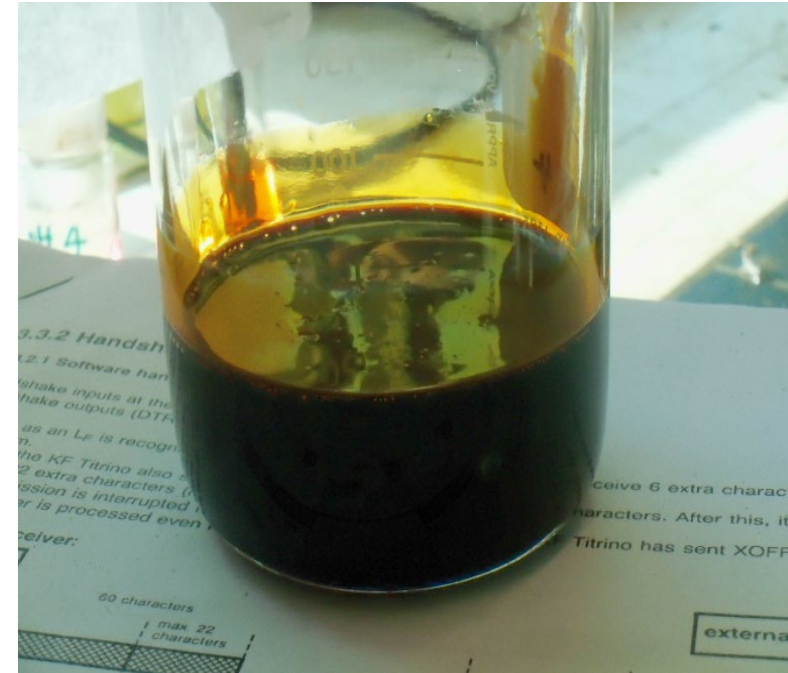
Reformulated Red mud catalyst



# Pinyon juniper red mud catalytic pyrolysis oils



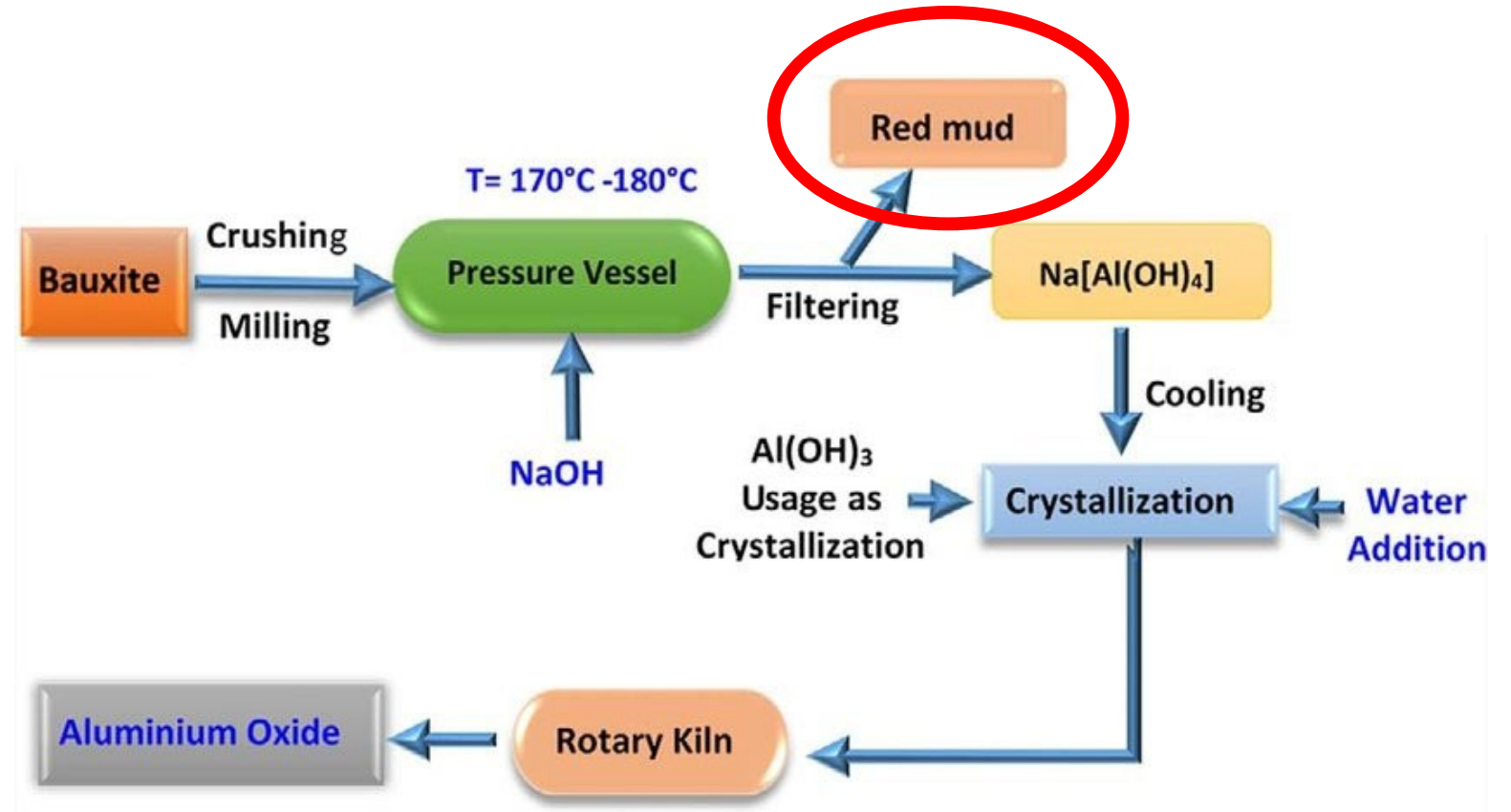
**Condenser oil**



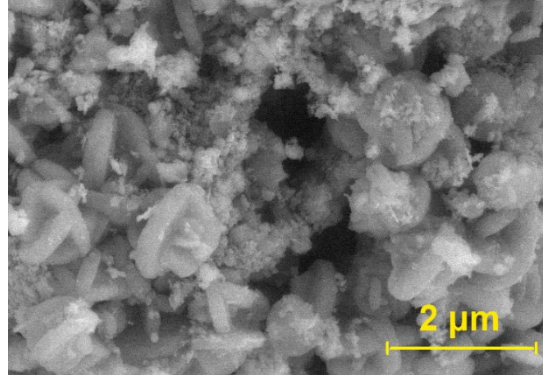
**ESP oil**

# Synthesis of new catalysts from Red Mud

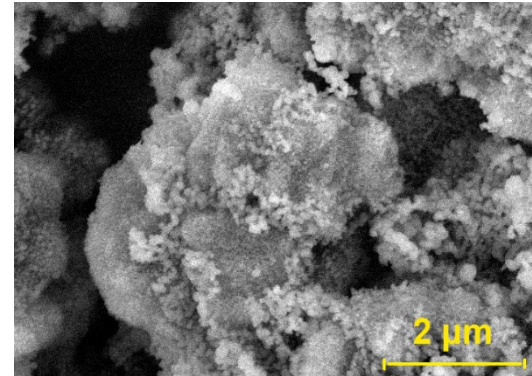
- What is Red Mud?
- Red mud problems



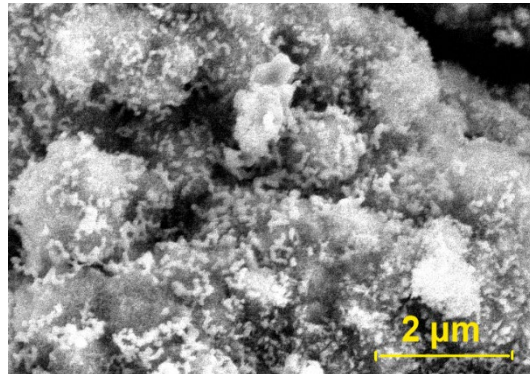
# Surface morphology – SEM images



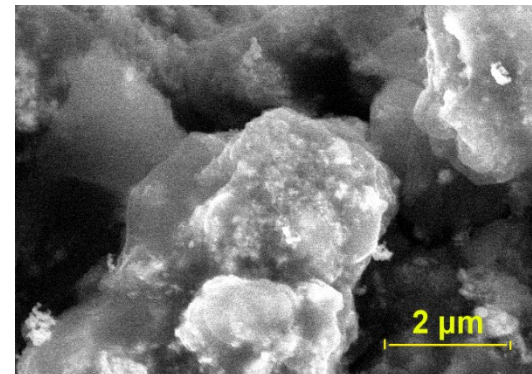
RM support



40%Ni/RM – Calcined



40%Ni/RM – Reduced form



Used (coked) Ni/RM



# Pyrolysis oil processing

- Traditional process: 3-step

1- Ketonization

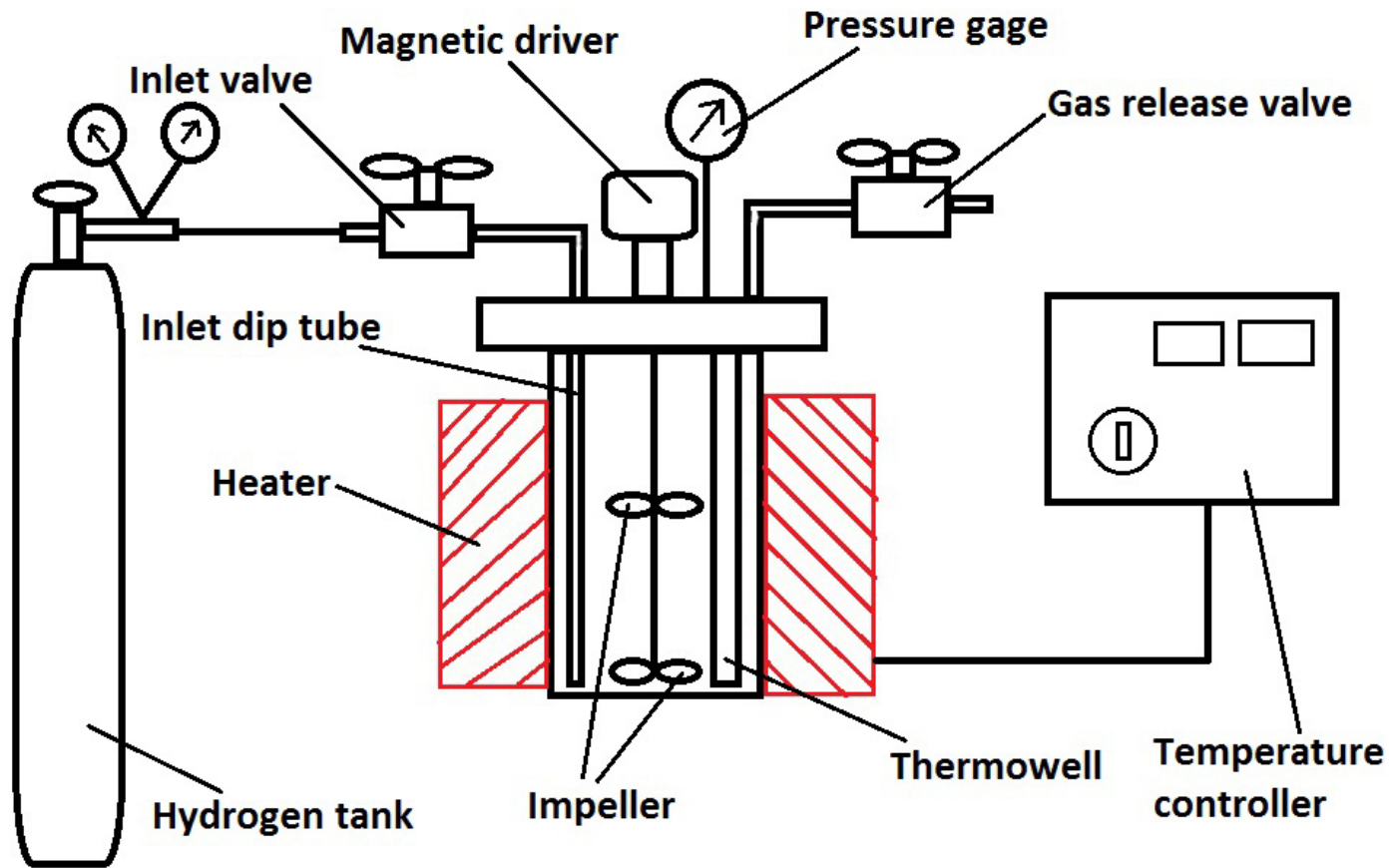
2- Aldol condensation

3- Hydrodeoxygenation

- **Our novel process:**

One-pot synthesis of hydrocarbons using multifunctional Ni/RM

# Hydrodeoxygenation reaction



## **Experimental condition:**

Reaction time = 30 minutes

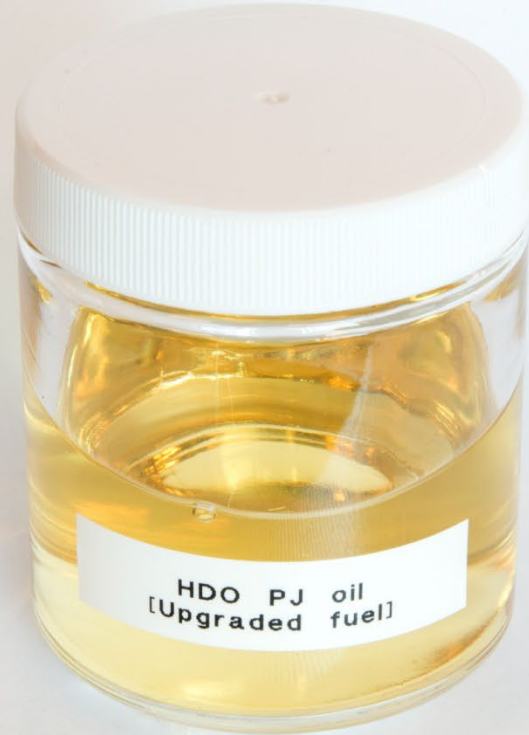
Temperature = 350 °C

H<sub>2</sub> cold pressure = 900 psi

85% water

Catalyst / reactant (wt./wt.) = 0.15

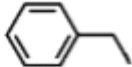
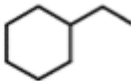
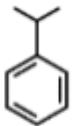
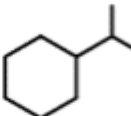
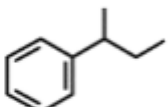


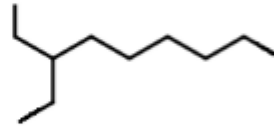

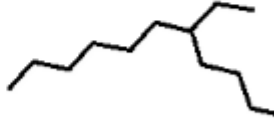
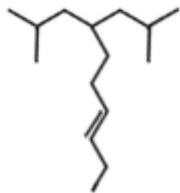
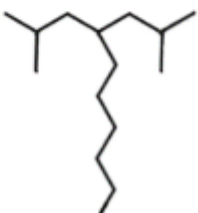




**Upgraded fuel**

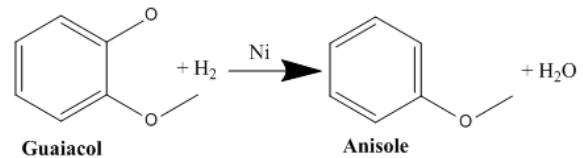
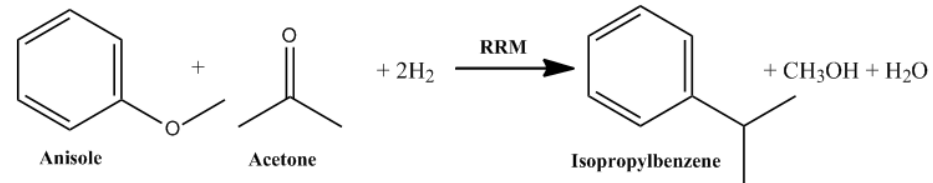
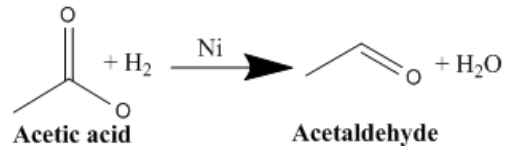
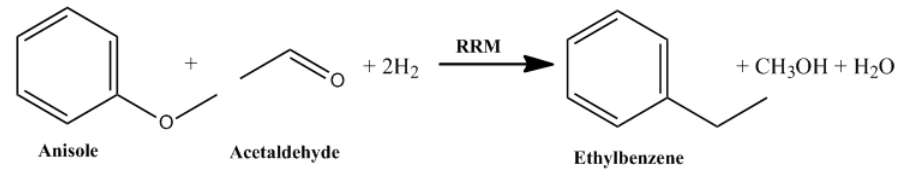
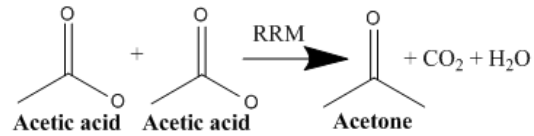
# Table of synthesized hydrocarbons (guaiacol reactions)

- Structures were confirmed using GC-MS and NMR

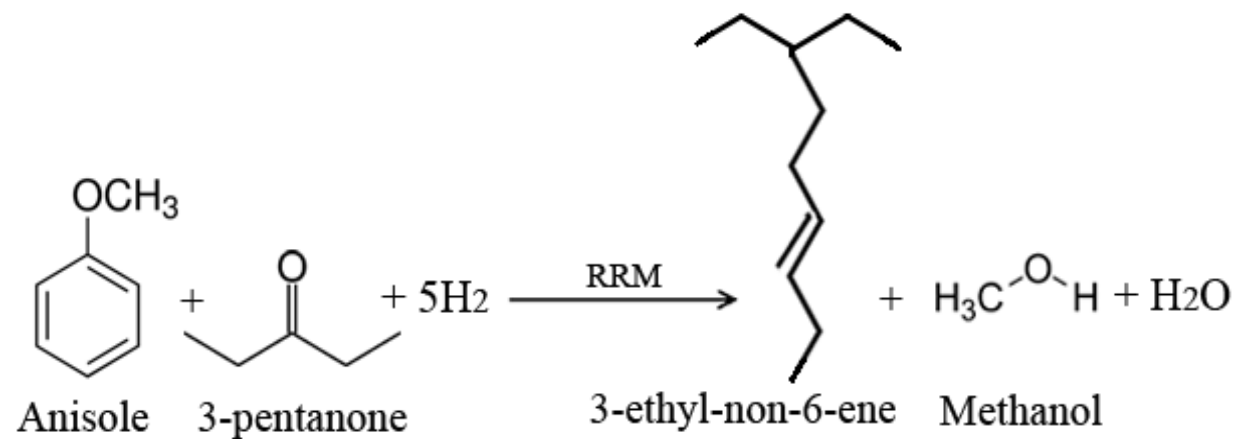
| Carbonyl alkylation products    |          |   | Hydrogenation products          |          |   |
|---------------------------------|----------|---|---------------------------------|----------|---|
| Formula                         | Catalyst | Structure   | Formula                         | Catalyst | Structure   |
| C <sub>8</sub> H <sub>10</sub>  | RRM      |    | C <sub>8</sub> H <sub>16</sub>  | Ni       |    |
| C <sub>9</sub> H <sub>12</sub>  | RRM      |    | C <sub>9</sub> H <sub>18</sub>  | Ni       |    |
| C <sub>10</sub> H <sub>14</sub> | RRM      |    | C <sub>10</sub> H <sub>22</sub> | Ni       |    |
| C <sub>11</sub> H <sub>22</sub> | RRM      |    | C <sub>11</sub> H <sub>24</sub> | Ni       |    |
| C <sub>13</sub> H <sub>26</sub> | RRM      |   | C <sub>13</sub> H <sub>28</sub> | Ni       |   |
| C <sub>15</sub> H <sub>30</sub> | RRM      |  | C <sub>15</sub> H <sub>32</sub> | Ni       |  |

# Synthesis of hydrocarbons: guaiacol reactions

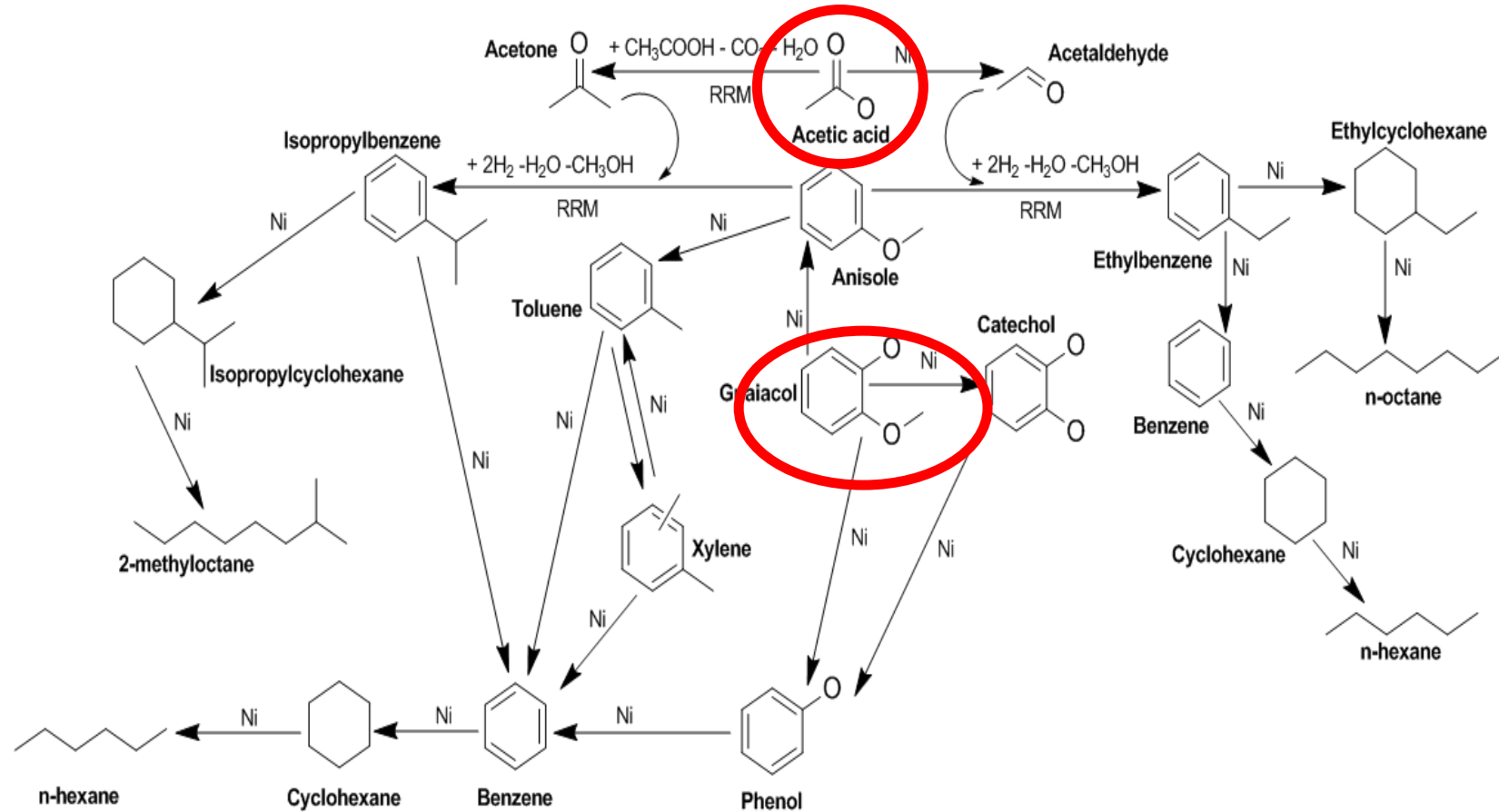
- Ketonization – partial reduction – carbonyl alkylation



# Synthesis of hydrocarbons: guaiacol reactions

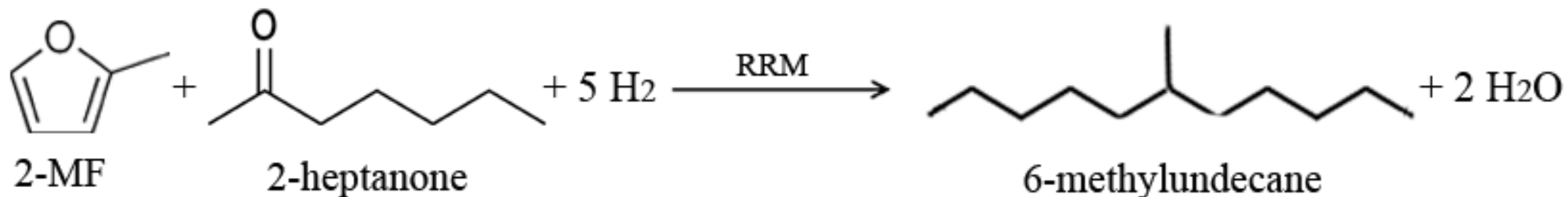
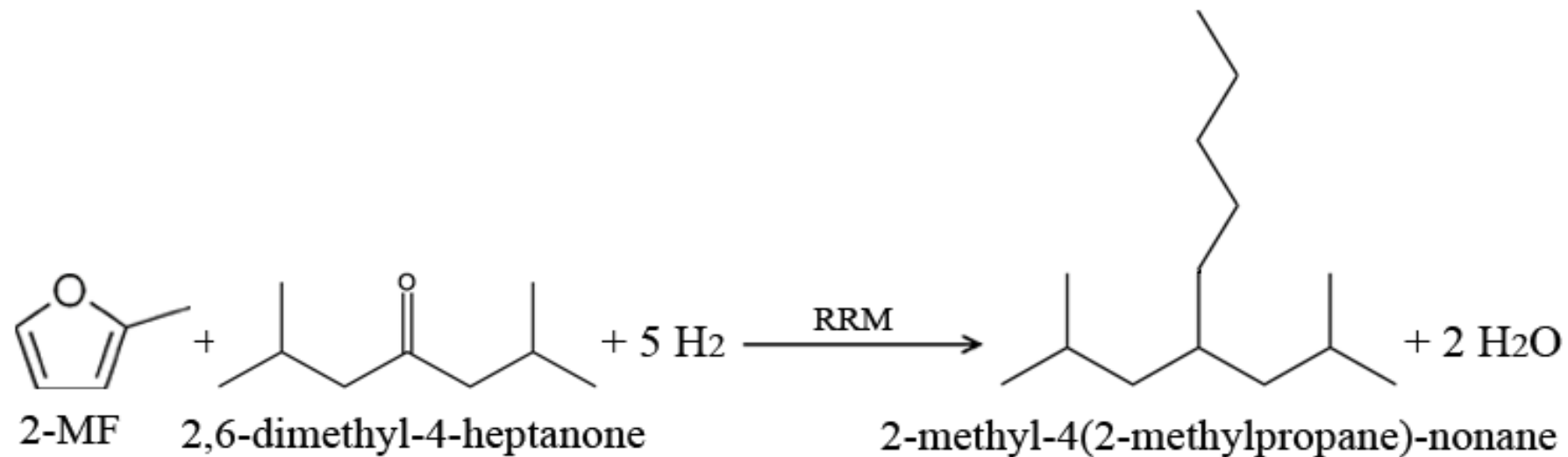


# Reaction network : Guaiacol-based (on Ni/RM)



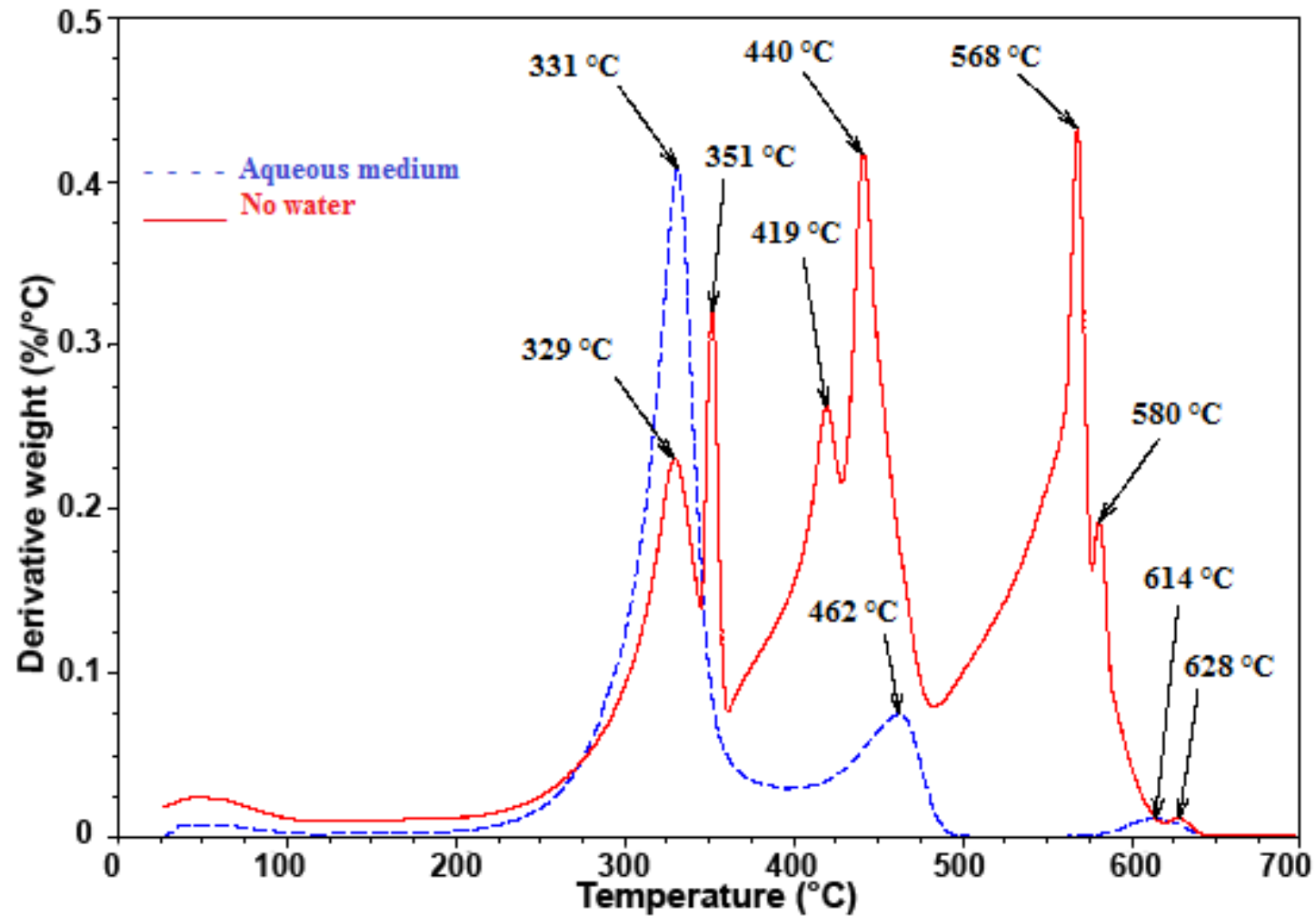
F.A. Agblevor, H. Jahromi "Aqueous phase synthesis of hydrocarbons from reactions of guaiacol and low molecular weight oxygenates", ChemCatChem.

# Synthesis of hydrocarbons: furfural reactions





# Effect of aqueous phase on coke formation



Reaction of **Guaiacol** + **Acetic acid**

# Conclusion

- One-pot carbonyl alkylation-hydrodeoxygenation for production of liquid hydrocarbons from catalytic pyrolysis oil was demonstrated
- Synthesis of C<sub>6</sub> to C<sub>15</sub> hydrocarbons through unique catalytic activity was the origin of the hydrocarbons from the catalytic pyrolysis oils
- The composition of the upgraded catalytic pyrolysis oil hydrocarbons were similar to those found in petroleum jet fuels
- Aqueous medium reduced coke formation and made separation of products very easy
- 100% conversion, high selectivity, and excellent yield were achieved

# Acknowledgement

- USTAR Program is acknowledged for funding support.
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**THANK  
YOU!**



# Upgrading techniques

- Bio-oil negative properties
- Steam reforming
- Supercritical fluids
- Esterification
- Hydrodeoxygenation (HDO)