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Catalytic property of olivine for bio-oil gasification

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CATALYTIC PROPERTY OF OLIVINE FOR BIO-OIL GASIFICATION

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POLYTECHNIQUE MONTRÉAL
LE GÉNIE EN PREMIÈRE CLASSE

Institute for Chemicals and Fuels from Alternative Resources
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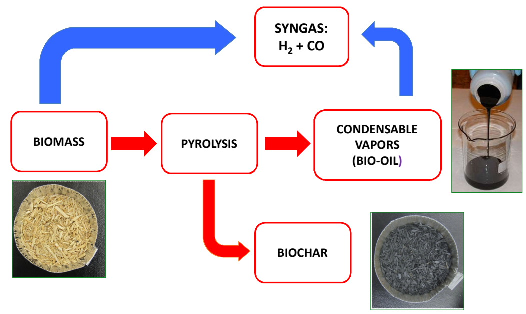
CONTEXT



A catalyst with an optimum formulation is required for maximum bio-oil conversion and yield of syngas with long enough stability against deactivation, attrition, …

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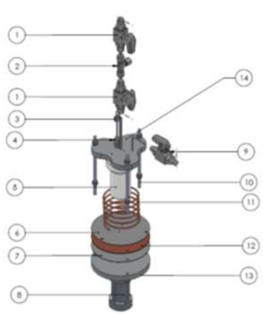
The Jiggle Bed Reactor (JBR)

1. on/off feed valves
2. Inlet of carrier gas
3. Thermocouple
4. Inlet of feed and carrier gas
5. Ceramic crucible with insulation
6. Insulation disk
7. Insulation disk
8. Linear pneumatic actuator
9. Outlet gas valve
10. Stainless steel support rods
11. Copper coil
12. Copper disk
13. aluminum disk
14. Stainless steel scalloped disk



M. Latifi, F. Berruti, C. Briens, AIChE Journal, 60(9), 3107-3122, 2014

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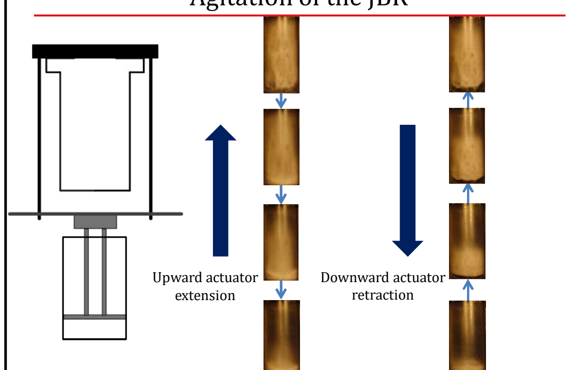
Agitation of the JBR



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Testing Catalytic Activity of Olivine : (Mg, Fe)$_2$SiO$_4$

- 4 µl bio-oil injected by capillary tubes
  → Dynamotive bio-oil (DMB) from hardwood
- No excess steam was used
- Bed materials= 10g:
  - → Silica sand for thermal cracking tests (106-212 µm)
  - → Pretreated olivines for catalytic tests (106-212 µm):
    - Olivine calcined with air at 1000°C for 24 h
    - Olivine calcined with air at 850°C for 24h
    - Olivine reduced in-situ with hydrogen at 800°C for 24 h
- Temperature: 800 °C, Reaction time: 10 to 600 s
- A micro GC was used to analyze the produced gases:
  → H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6

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Thermodynamic Model:
Equilibrium Constant Approach

Assumption: Input reactants and output products of bio-oil (CH_mO_n) gasification are related with the following equation:

$$CH_mO_n + b_1H_2O + b_2O_2 \rightarrow a_1H_2 + a_2CO + a_3CO_2 + a_4CH_4 + a_5H_2O_{(g)} + a_6C + a_7C_2H_6 + a_8C_2H_4 + a_9C_3H_{10} + a_{10}C_3H_8$$

Independent reactions between gasification products:

$$CH_4 + H_2O_{(g)} \leftrightarrow CO + 3H_2$$
$$C_2H_6 + 2H_2O_{(g)} \leftrightarrow 2CO + 5H_2$$
$$C_2H_4 + 2H_2O_{(g)} \leftrightarrow 2CO + 4H_2$$
$$C_3H_8 + 3H_2O_{(g)} \leftrightarrow 3CO + 7H_2$$
$$C_3H_6 + 3H_2O_{(g)} \leftrightarrow 3CO + 6H_2$$
$$CO + H_2O_{(g)} \leftrightarrow CO_2 + H_2$$
$$C + H_2O_{(g)} \leftrightarrow CO + H_2$$

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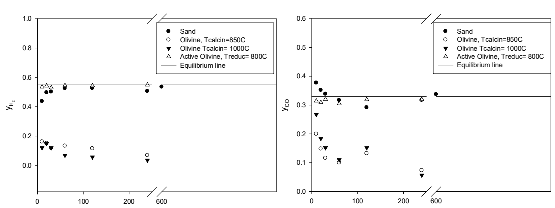
Experimental vs. Equilibrium Mole Fractions



- <u>Sand:</u> Mole fractions tend to reach equilibrium after 600 s
- <u>Reduced Olivine:</u> Mole fractions reach equilibrium quickly
- <u>Calcined Olivines:</u> Mole fractions tend to ***decrease*** versus residence time and reach new equilibrium state

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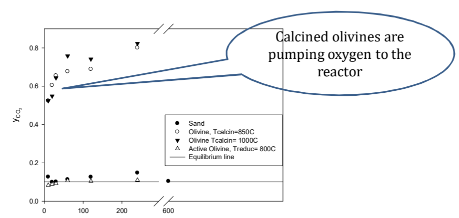
Experimental vs. Equilibrium Mole Fractions



- <u>Sand:</u> Mole fractions tend to reach equilibrium after 600 s
- <u>Reduced Olivine:</u> Mole fractions reach equilibrium quickly
- <u>Calcined Olivines:</u> Mole fractions tend to ***increase*** versus residence time and reach new equilibrium state

✓ Added oxygen to the reactor from olivine calcined at 1000 °C was estimated to be 1.96 times as large as oxygen mass in bio-oil after a 240 s reaction time

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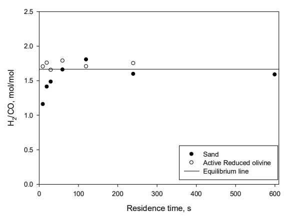
Experimental vs. Equilibrium H_2/CO Ratio

- ✓ The predicted molar H_2/CO ratio was 1.65 without the addition of extra steam
- ✓ It was predicted that molar H_2/CO ratio of 2 can be obtained at 800°C when additional 0.344g steam per g of bio-oil is fed



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Conclusion

- Reduced olivine was an active and suitable catalyst in term of maximum syngas yield and bio-oil conversion
- Calcined Olivine had detrimental effect on syngas yield
- However, tests with calcined olivine revealed that it can be utilized as an oxygen carrier in chemical looping gasification processes