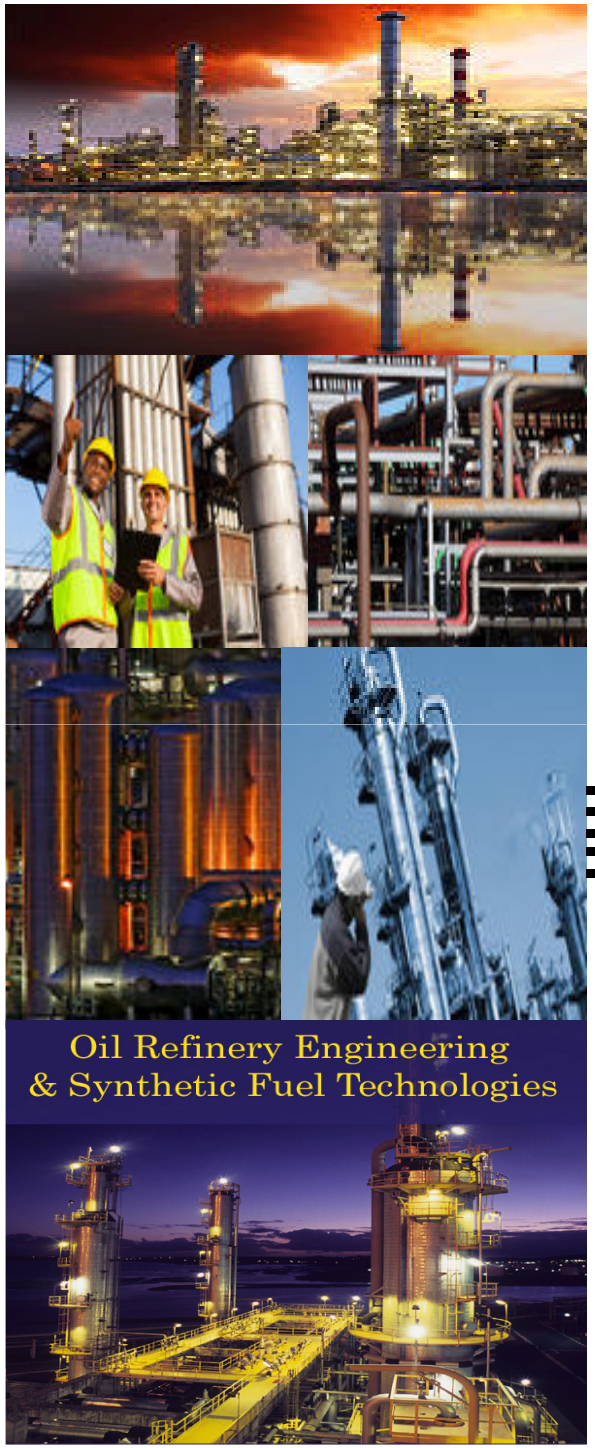
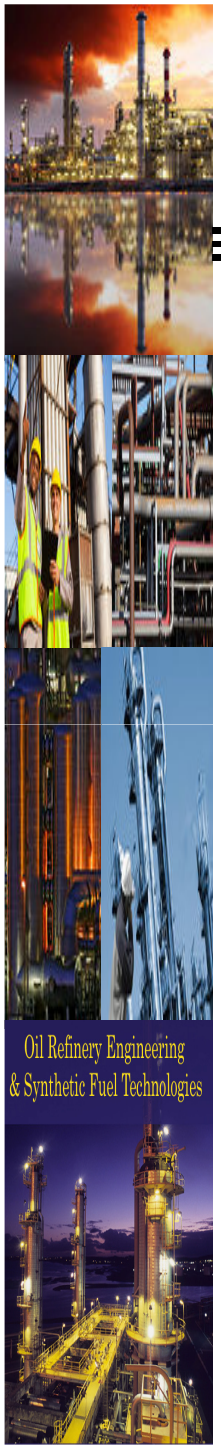



# Solvothermal Production of Biofuels from Fructose

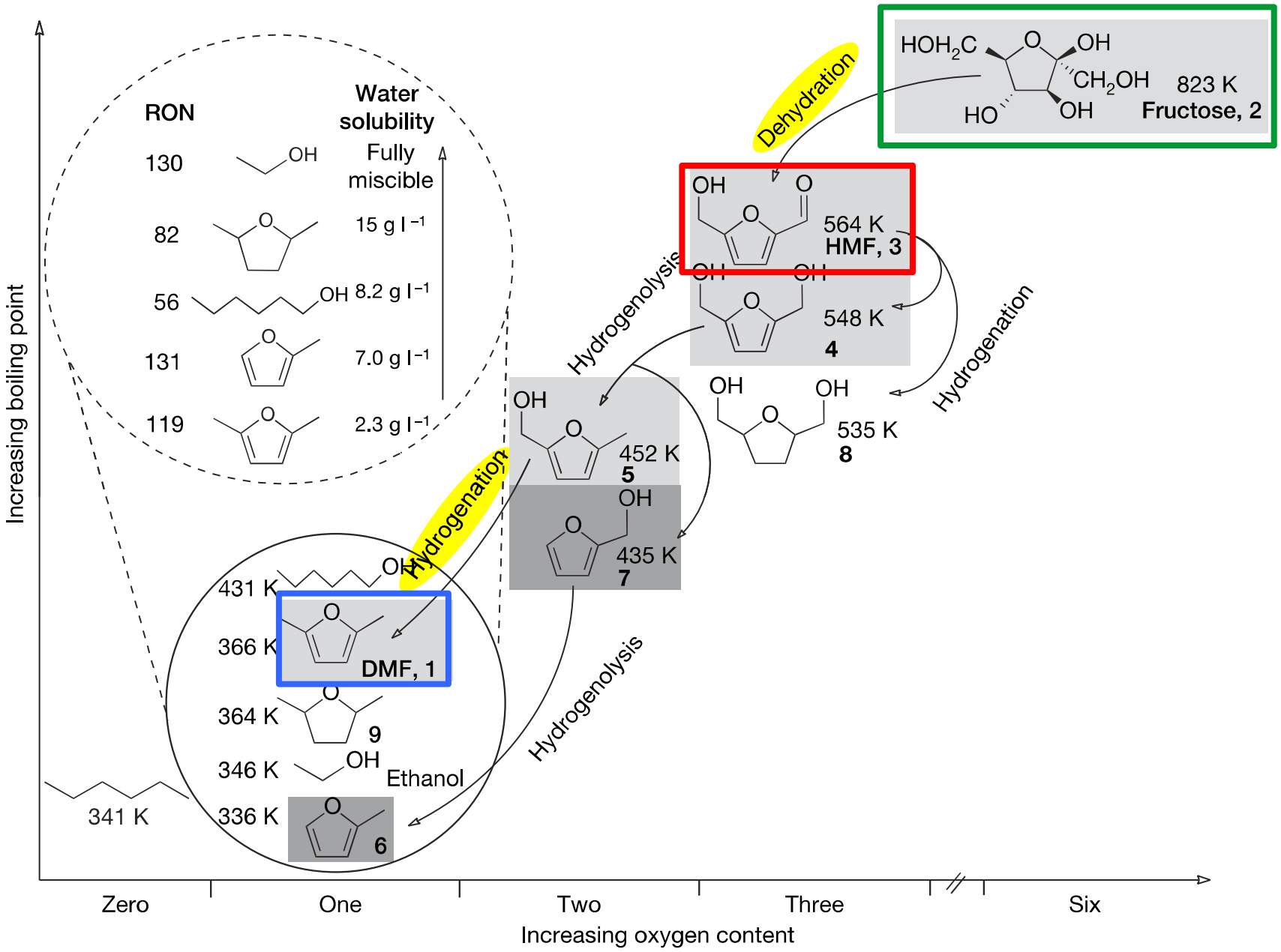
*Bushra Al-Duri*

School of Chemical Engineering
University of Birmingham
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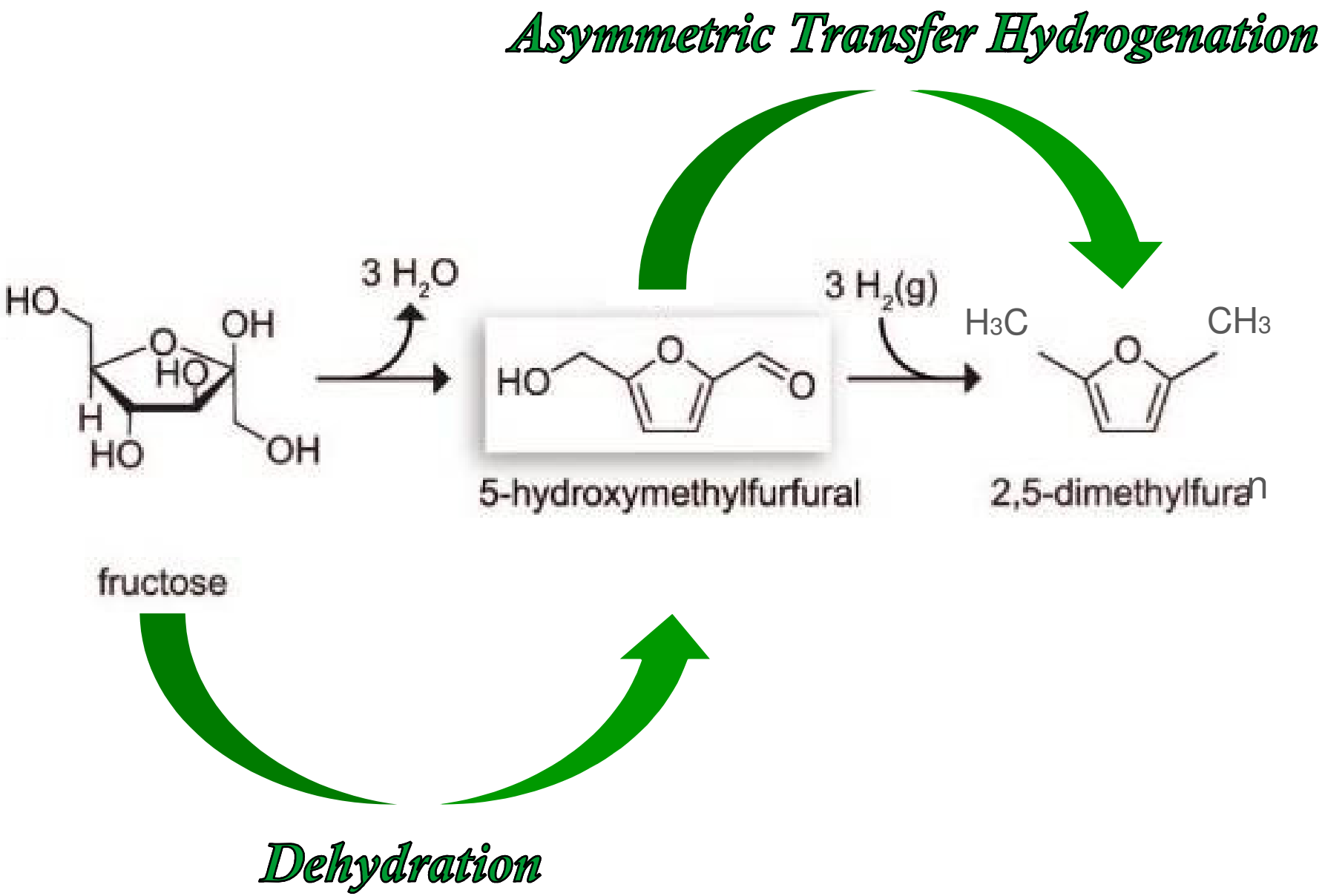


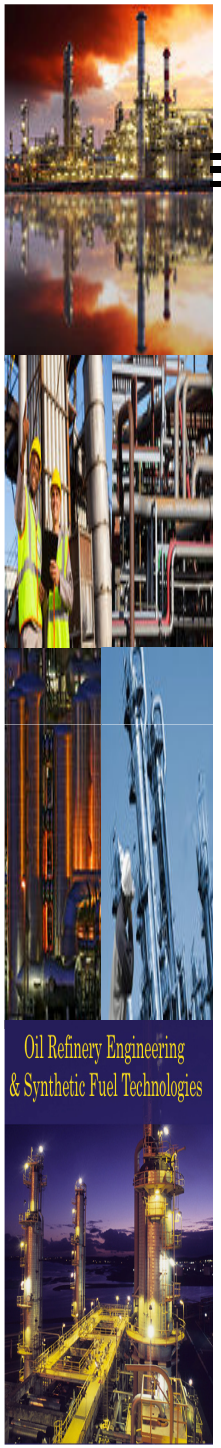

# STRUCTURE

- Biofuel components: definition & advantages.
- Production of 2,5-DMF from HMF.
- Production of HMF from C6 sugars.
- Future Work.




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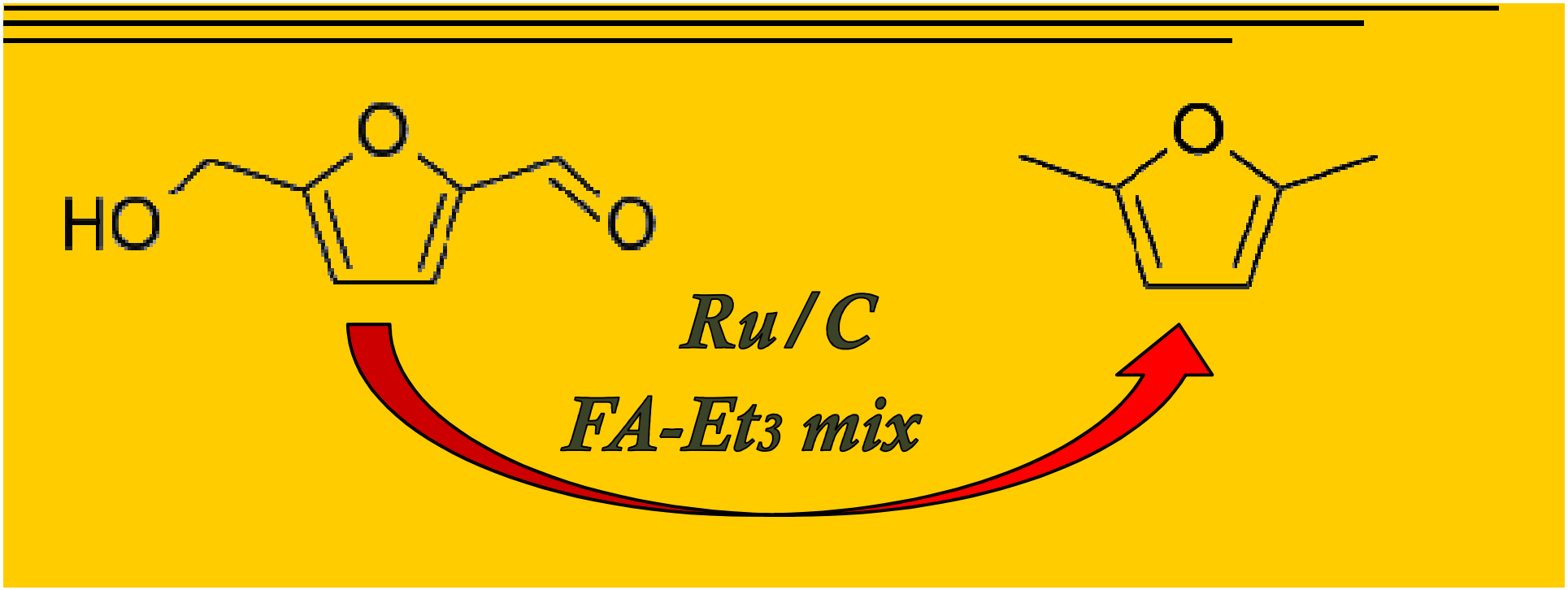

Asymmetric Transfer Hydrogenation
3 H2O
3 H2(g)
HO
OH
O
HO
H
HO
OH
HO
O
O
H3C
CH3
O
5-hydroxymethylfurfural
2,5-dimethylfuran
fructose
Dehydration

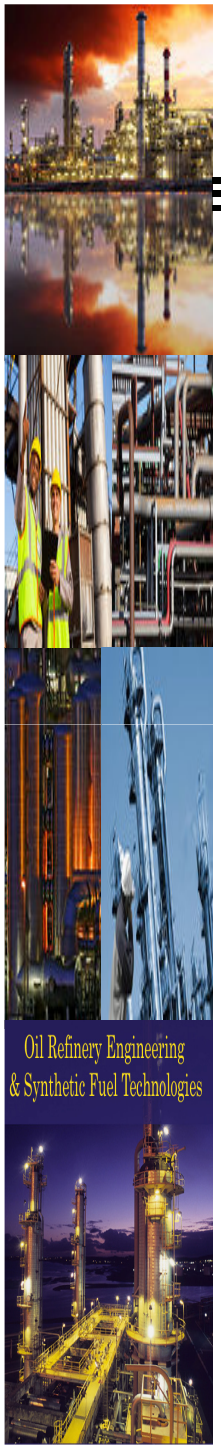



# Why 2,5 DMF ?

- High boiling point [92°C]; 14°C higher than ethanol's (78°C).
- High energy density [30 kJ $cm^{-3}$]; 40% higher than ethanol's.
- High Octane Number [RON = 119]; close to that of gasoline.
- Immiscible with water: no absorption of moisture & easier to blend with gasoline than ethanol.
- Similar combustion properties to gasoline; thus adoptable with current spark-ignition engine technologies.
- Dual-injection strategy offers efficient and flexible use of biofuels, whilst still using gasoline.
- Production of DMF does not require energy crops.

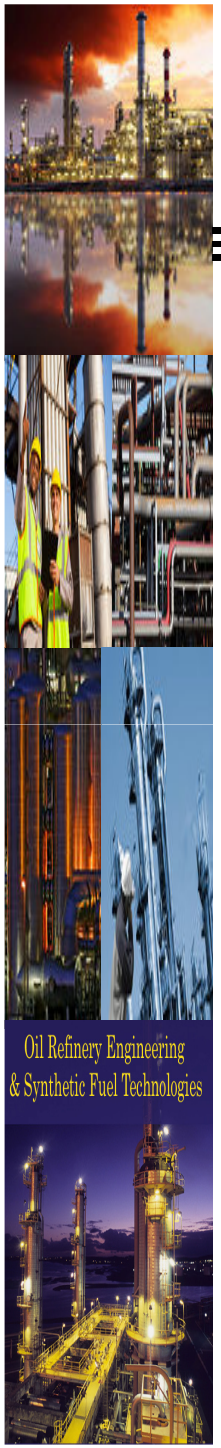
# Catalytic Hydrogenation of 5-HMF in Formic acid – Triethylamine Mixture to produce 2,5 Dimethyl furan (DMF).






# Selection of Catalyst & Reagents

- *Ru, Rh & Ir* are best catalysts for *Asymmetric Transfer Hydrogenation* (ATH). *Ru (II)* proved most successful for aldehydes & ketones.
- Metal catalyzed ATH reactions were conducted in the mixture of HCOOH (*FA*) & tri-ethylamine ($NEt_3$), where the mix acts both as solvent & reductant.
- $FA/NEt_3$ mix forms a complex with *Ru(II),* which improves conversion and accelerates the reaction.
- **This work extends the use of catalyst/reagents combination from aldehydes & ketones reactions to the ATH of 5-HMF**.

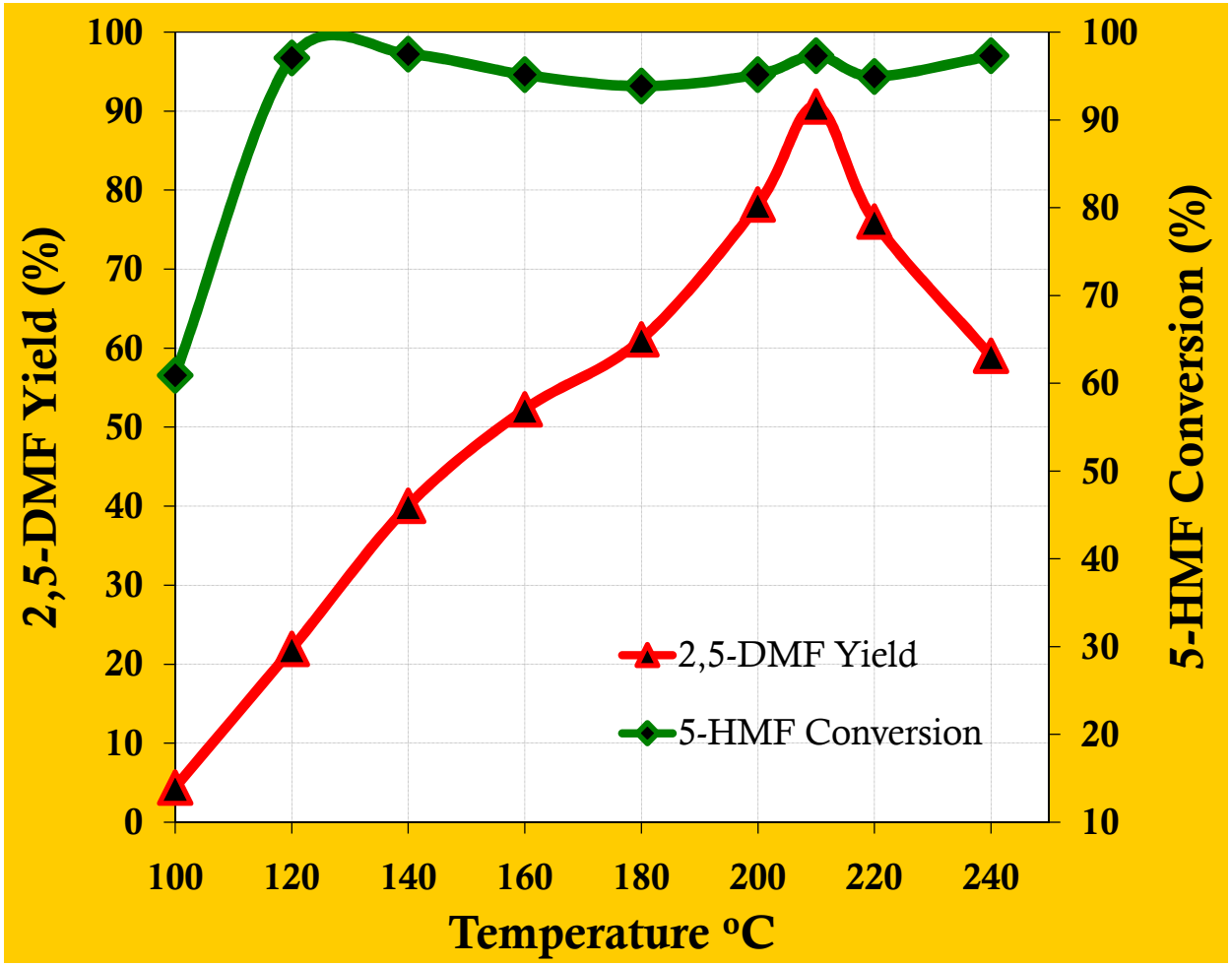



# Experimental Conditions

| | |
|---|---|
| **Temperature T, ° C** | 100 - 240 |
| **Reaction Time *t*, h** | 1 - 10 |
| ***FA: Et*$_3$ ratio** | 1:1 – 4:1 |
| **Ru/C catalyst dosage, g** | 0.05 – 5.0 |
| **[HMF]$_0$, M** | 0.2 – 1.4 |
| **Agitation speed, rpm** | 100 - 700 |

*[HMF]$_0$ = 0.8 M, t = 4 h; Ru/C (5 wt%) = 0.1g; FA+Et$_3$ volume = 25mL; FA:TEA = 5:2, rpm = 300, T = 210 ° C*

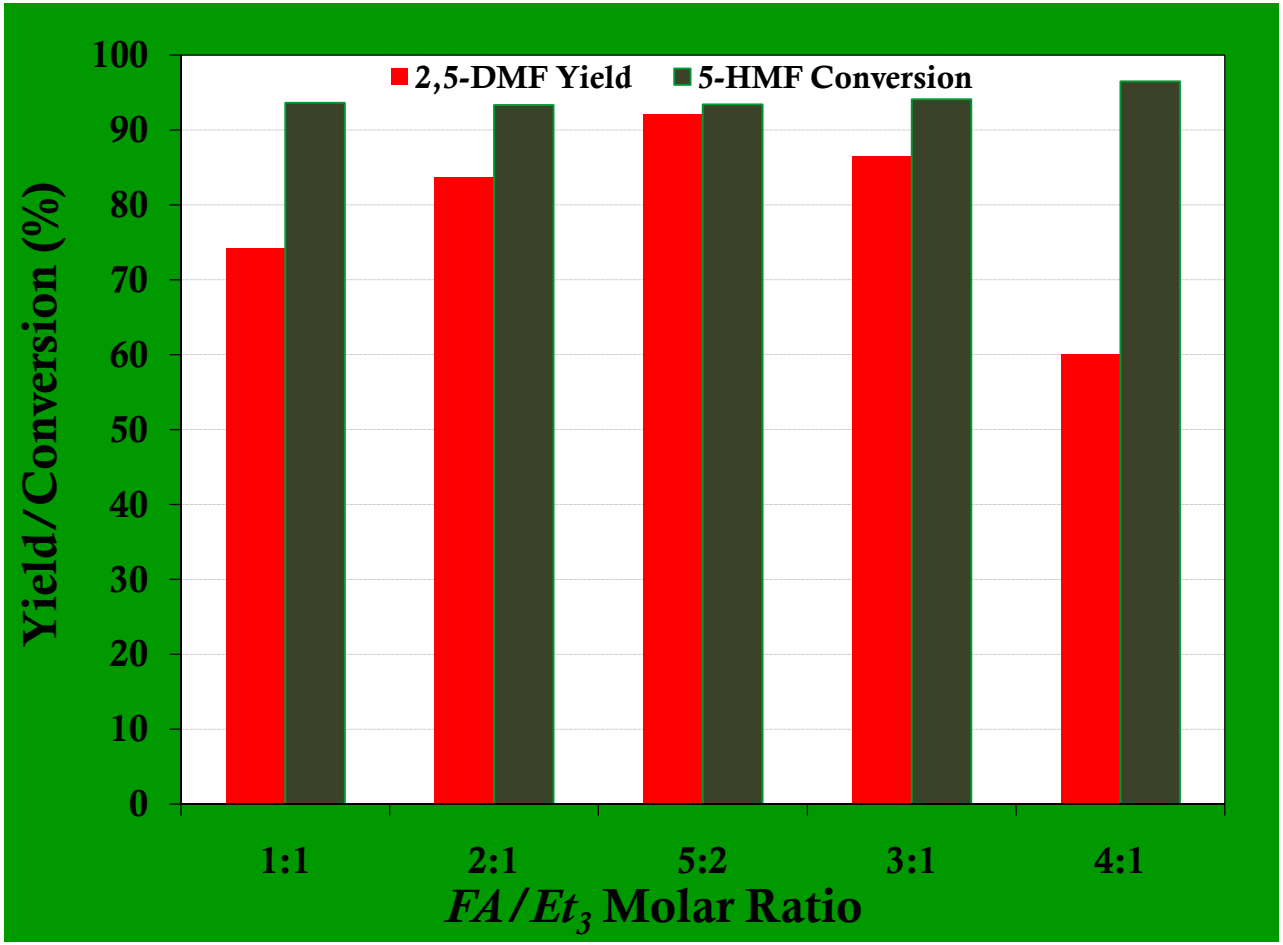
# The Effect of Temperature




- T = 210° C gave the best HMF conversion of 97.3% & DMF yield of 90.6%.

- The observed decrease after 210°C was attributed to further conversion of DMF to other side-products.

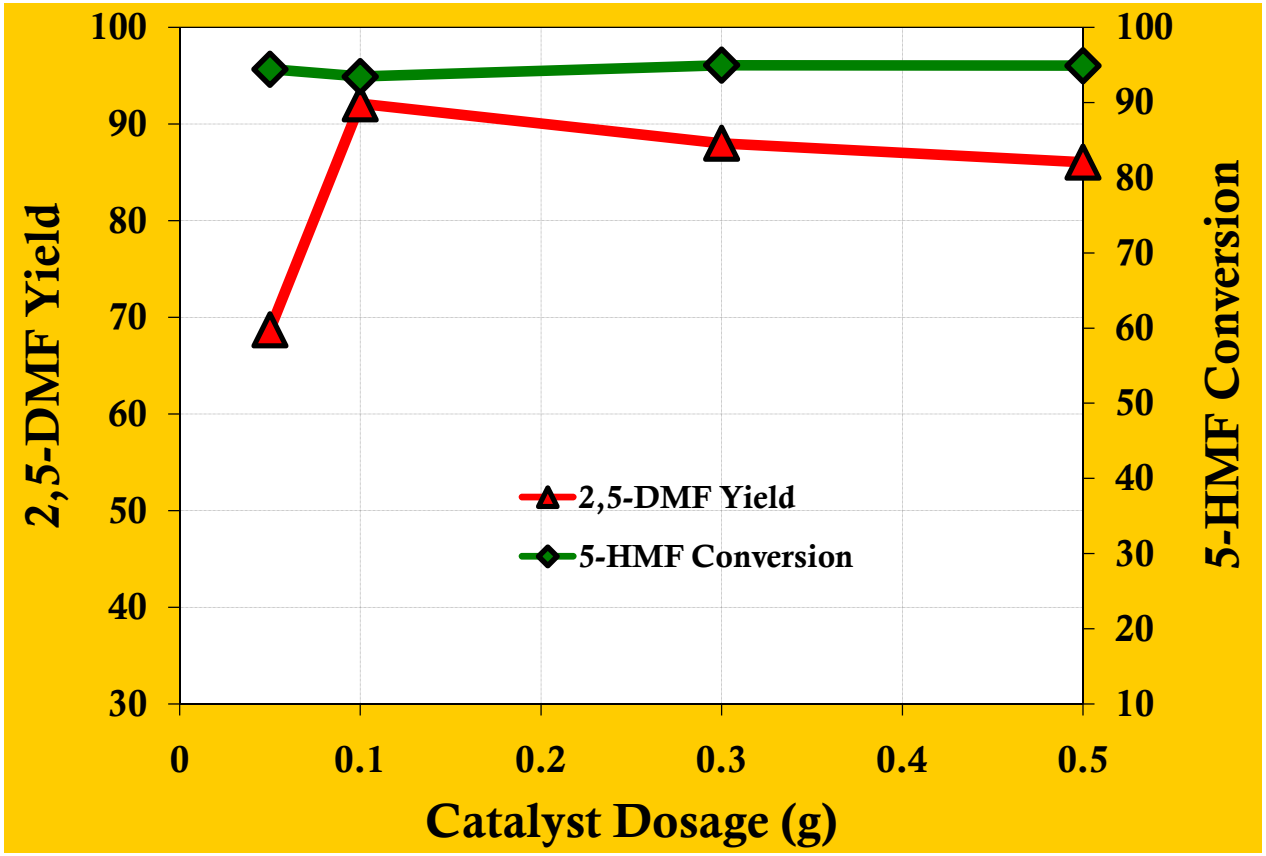
# The Effect of $FA/Et_3$ Ratio




- 5:2 ratio gave 93.8% HMF conversion & 92.1 & DMF yield.

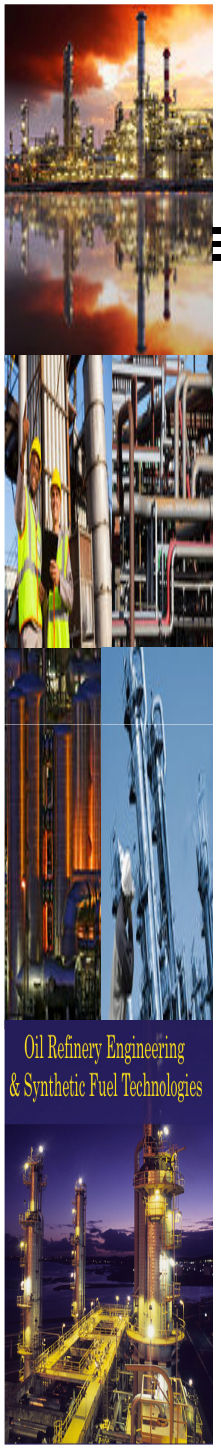
- *FA* is the H donor in this reaction.
- $Et_3$ is a base, used in organic synthesis.
- $FA/Et_3$ mix facilitated the H transfer process by acting as reductant.

# The Effect of Ru/C Dosage




- *Ru (II)* forms a complex with $FA/Et_3$ mix, thus excess *Ru (II)* offers no advantage.

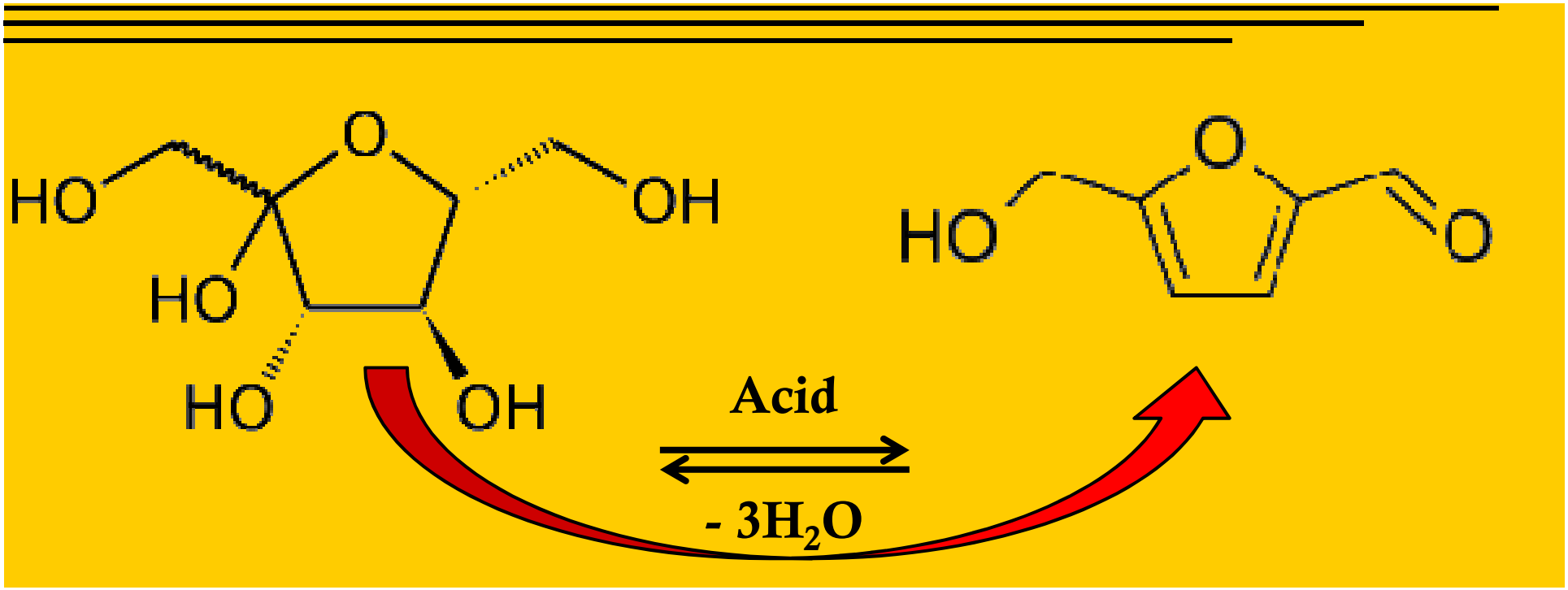
- DMF yield is a function of [HMF]/unit mass of catalyst. Thus, as mass of catalyst increases above 0.1g, HMF/DMF ratio decreases and so does the yield.

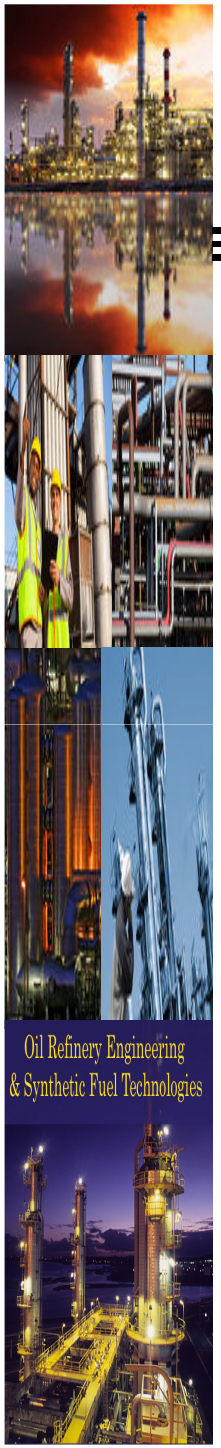



# Conclusions (1)

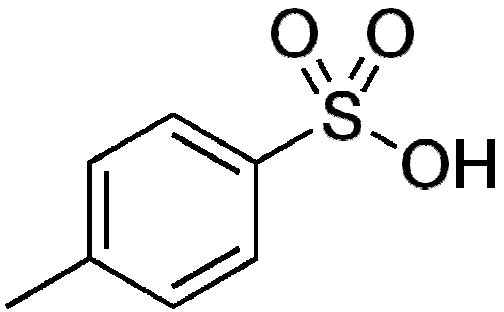
- 97.3% HMF conversion, giving DMF yield of 92.1% was successfully achieved in a batch reactor operating at optimum reaction conditions.
- Best reaction conditions are: 210°C , 0.8 M HMF, *FA/Et*$_3$ molar ratio of 5/2 using 0.1 g of *Ru (II)*, 300rpm, for 4h reaction time.
- *FA/Et*$_3$ mixture combined with *Ru (II)* form a green solvent-catalyst mix to enhance the production of DMF from HMF by ATH.

# Hydration of Fructose to produce 5-HMF using Deep Eutectic Mixture *p*-TSA+ChCl (*p*-toluene sulfonic acid + Choline Chloride)



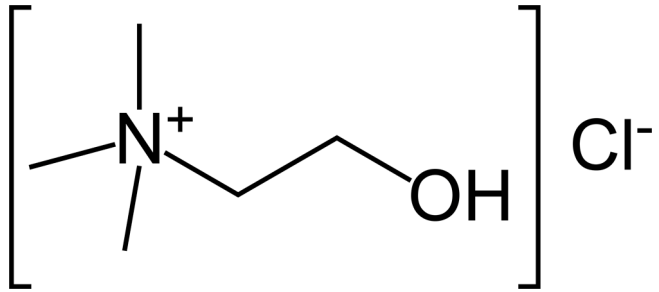



# Selection of Catalyst & Reagents



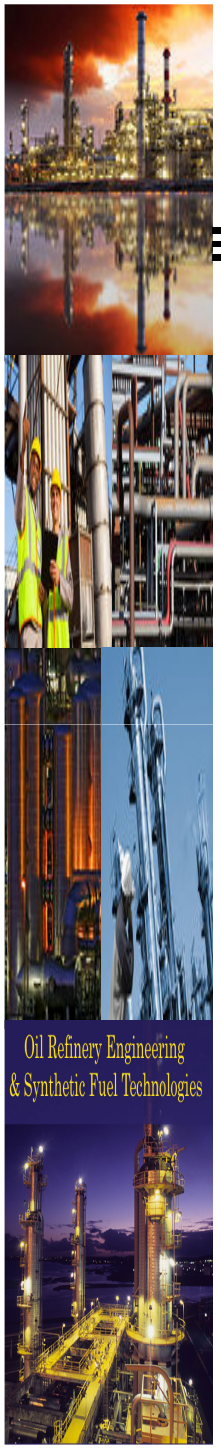

*p* - TSA

&




*Choline Chloride*

- Brønsted acidic deep-eutectic mixture dehydration of fructose to 5-HMF.
- The use of ChCl/*p*-TSA played a dual role both as hydrogen bond donor & catalyst for the dehydration reaction, thus obviating the addition of an external acid.




# Experimental Conditions

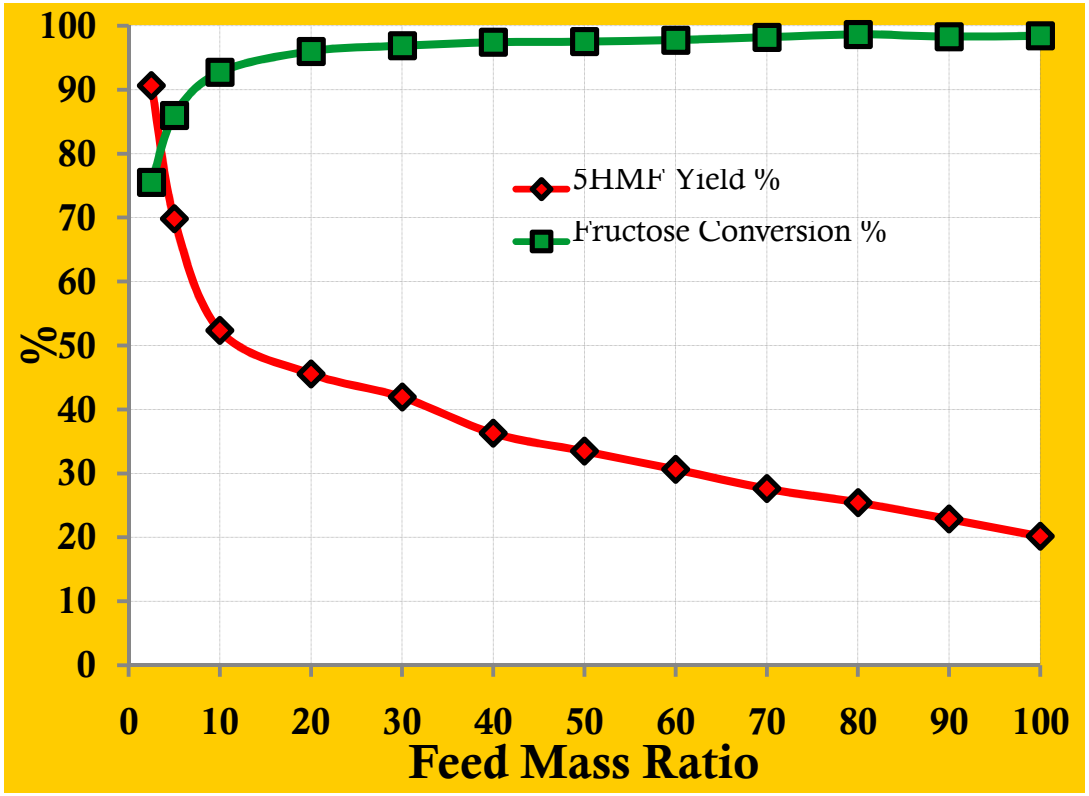
| | |
|---|---|
| Temperature[1], °C | 50 - 110 |
| Reaction time, min | 10 - 120 |
| Feed mass ratio[2], % | 2.5 - 100 |
| DES ratio[3], % | 1:0.5, 1:1, 1:1.5, 1:2 |

*[1] T = 80 °C, t = 60 min, Feed mass ratio = 5 %, DES ratio = 1:1.*

*[2] Weight percentage fructose in feed.*

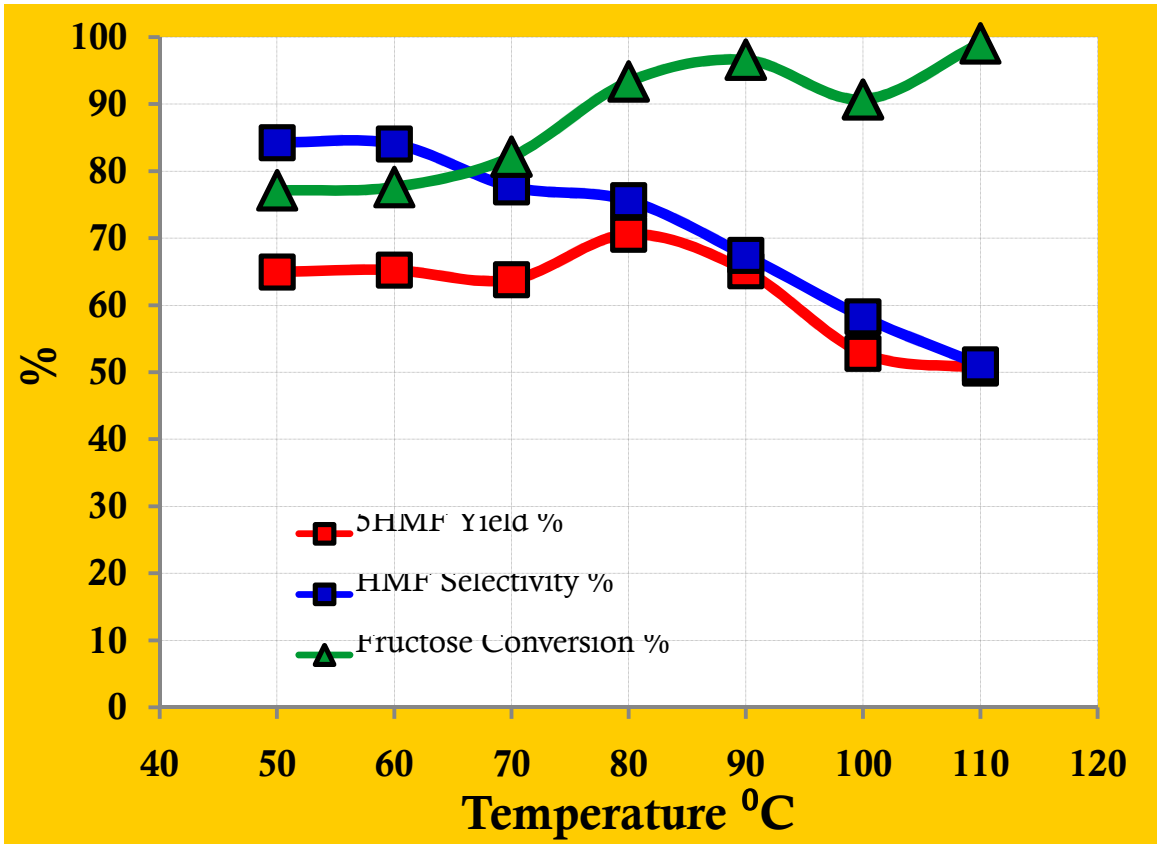
*[3] mixing molar ratio [ChCl:p-TSA].*

# Effect of mass feed ratio



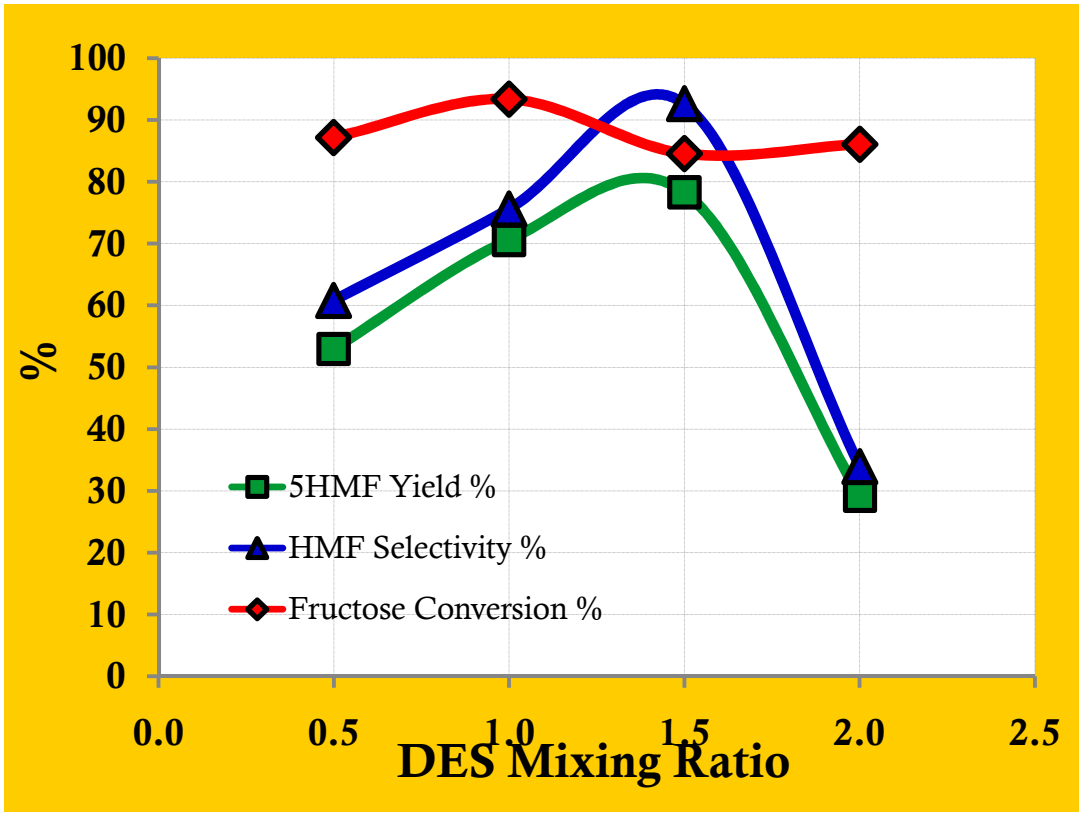

- 5HMF yield % decreased with increased fructose mass ratio.
- 5HMF is rehydrated by the presence of water produced from the dehydration of fructose.
- The lowest yield was 20.5% at feed ratio of 100%. High fructose concentration could result in unwanted side reactions.
- Change of the sample colour to a darker brown by increasing fructose ratio was observed.

# Effect of temperature

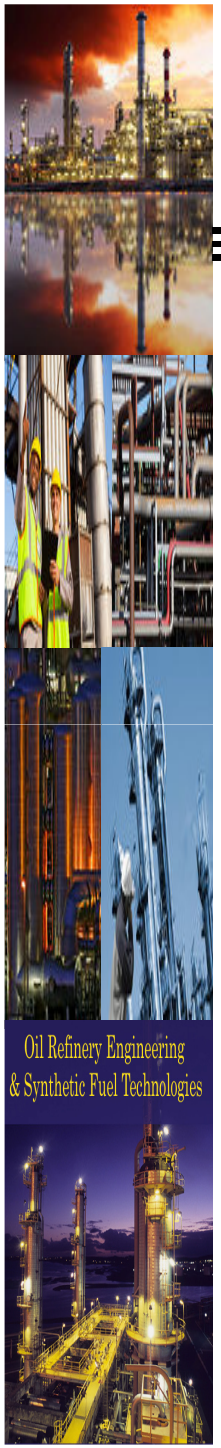



- Fructose conversion increased with temperature from 77.1% at 50 $^{0}$C to 99% at 110 $^{0}$C.
- 5HMF yield remained steady ≈ 65% up till 70 $^{0}$C then increased to 70.6% at 80 $^{0}$C.
- 5HMF selectivity decreased with temperature, from 84.3% at 50 $^{0}$C to 51.1% at 110 $^{0}$C. This is subsequent to decrease in yield caused by formation of side products at higher temperatures.

# Effect of DES mixing ratio

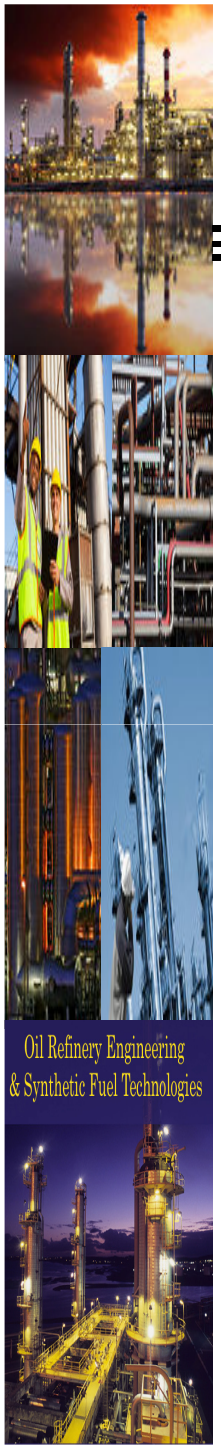



- maximum 5HMF yield of 90.7% was obtained at 1:1 DES molar mixing ratio. It decreased to 58.4% when the DES molar mixing ratio was increased to 1:1.5.




# Conclusions (2)

- DES mix of ChCl/*p*-TSA is a promising catalytic solvent mixture for the dehydration of fructose to 5HMF, giving high yields and selectivity.
- The best yield was obtained 90.7%; at feed ratio of 2.5w%, DES mixing molar ratio of 1:1, 80 $^{0}$C and 1h.




# Future Plans

- **Science-based investigations**
  - Investigations into the reaction pathway(s) for ATH and hydration.
  - Catalyst reusability studies.
- **Engineering-based investigations**
  - From batch to continuous systems.
  - Product separation & purification.
  - Combining both processes in one continuous process.
  - Product characterisation studies (combustion characteristics & engine performance, etc…)

*Thanks for your attention!*

*Questions?*

