Ethanol to LPG: the journey to a pilot plant and some of the challenges

TC Biomass 2024

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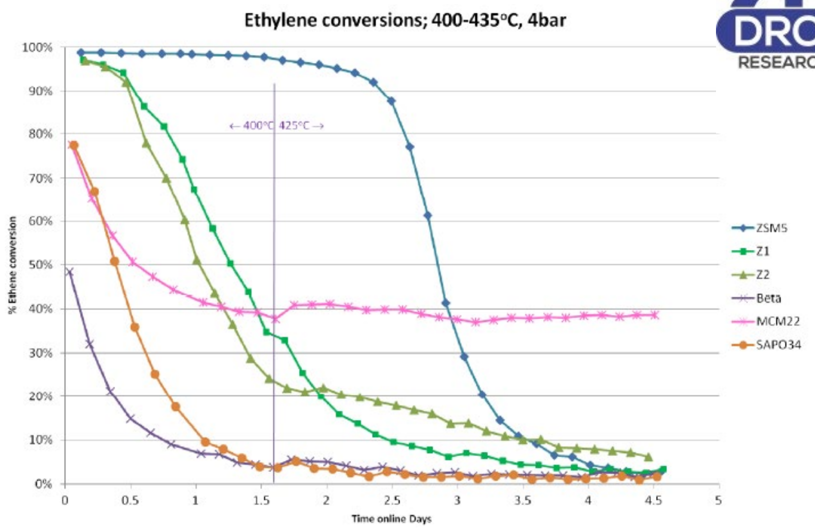
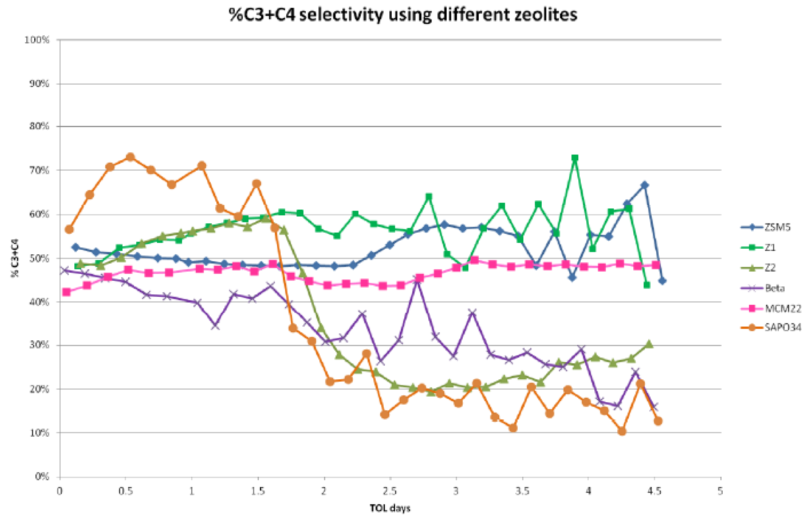
How did the journey start?

- Methanol-to-Propylene (MTP) or the **Ethylene-to-Propylene (ETP)** are very well-known processes

- Why not try Ethylene to LPG without adding any H_2?

- Performance of majority of the zeolites were falling off after 4 days, with ZSM-5 the most promising due to stability and selectivity towards paraffinic C_3 and C_4. MCM 22 produced mainly Propene instead of Propane





Screening the conversion of Ethylene to LPG over catalyst candidates. (Note only conversion to C_3 and C_4 shown)

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Why not starting from Ethanol?

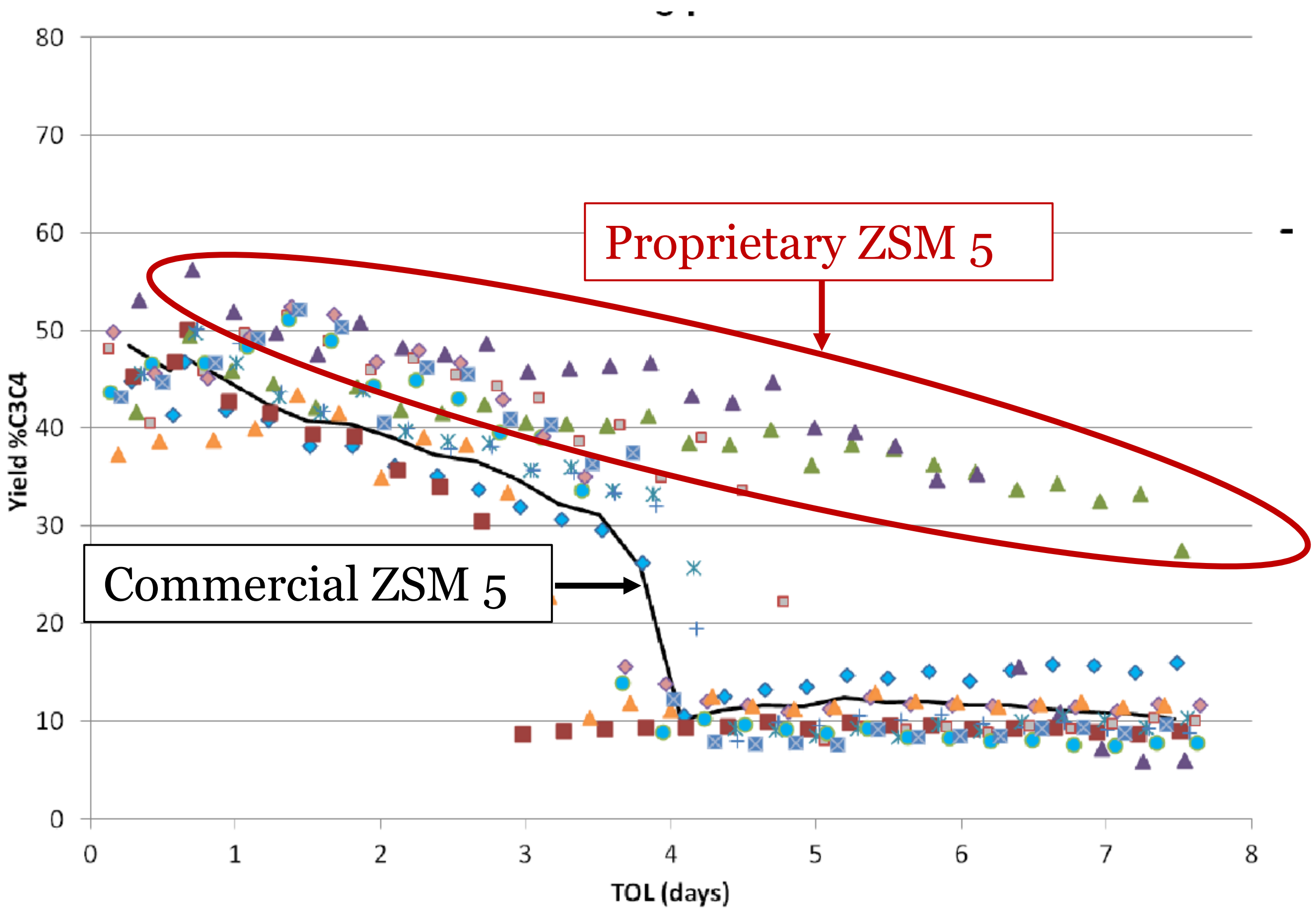
- Ethanol can be dehydrated to produce Ethylene
- Potential for up to 35 million tonnes BioLPG from existing global Ethanol

Region	Million Gallons	Million Tonnes	Percentage
US	**15,620**	**46.7**	**53%**
Brazil	**8,260**	**24.7**	**28%**
EU	1,440	4.3	5%
India	1,430	4.3	5%
China	950	2.8	3%
Canada	460	1.4	2%
Thailand	370	1.1	1%
Argentina	300	0.9	1%
Rest of the world	760	2.3	3%
Total	29,590	88.4	

Source RFA 2023

Screening catalysts

- Several modified H-ZSM 5 catalysts have a rapid decrease in C_3 and C_4 selectivity
- Certain (proprietary) catalysts (green and purple triangles) maintained reasonable selectivity to LPG after 4 days
- Proprietary catalyst produce more (desired) paraffinic compounds than olefinic



Screening the conversion of Ethanol to LPG over catalyst candidates. (Note only conversion to C_3 and C_4 shown)

Catalyst stability tests

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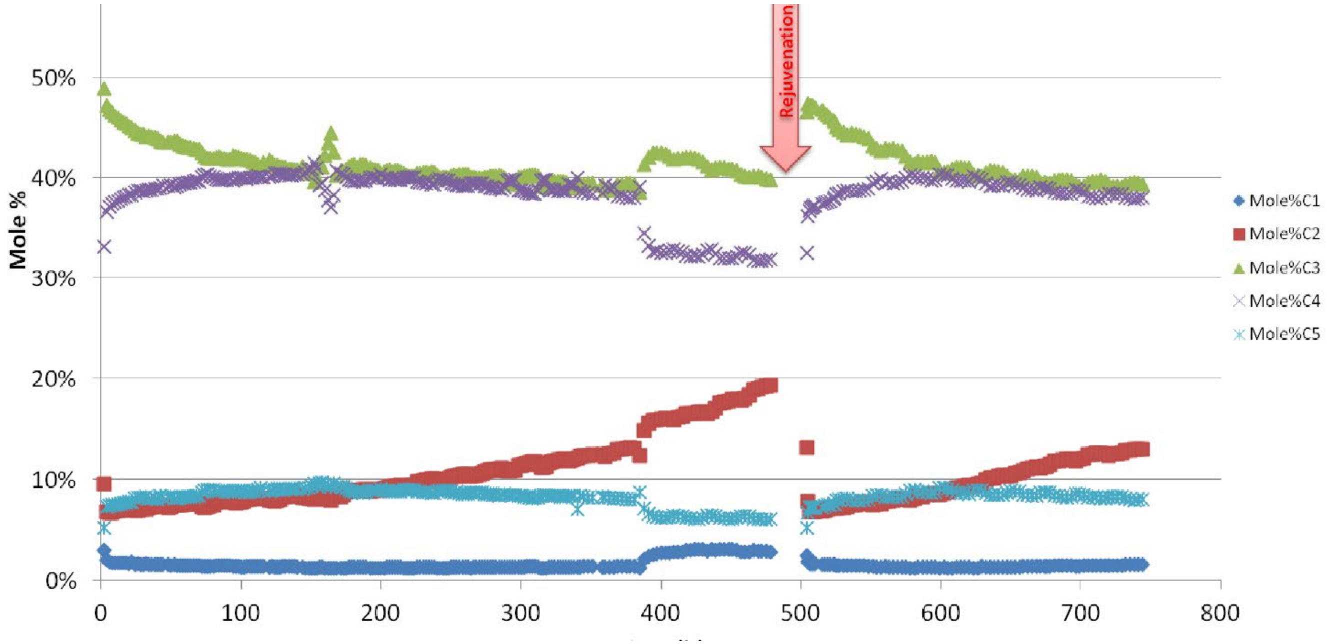
- Catalyst stability was tested for more than 700 hours
- Air rejuvenation was also tested recovering catalyst performances back
- An increase in Ethylene formation was a leading indicator of catalyst deactivation



Stable two weeks operation of conversion of Ethanol to LPG over proprietary catalyst. (Forced conditions at 400 hours leading to a successful air regeneration at 500 hours)

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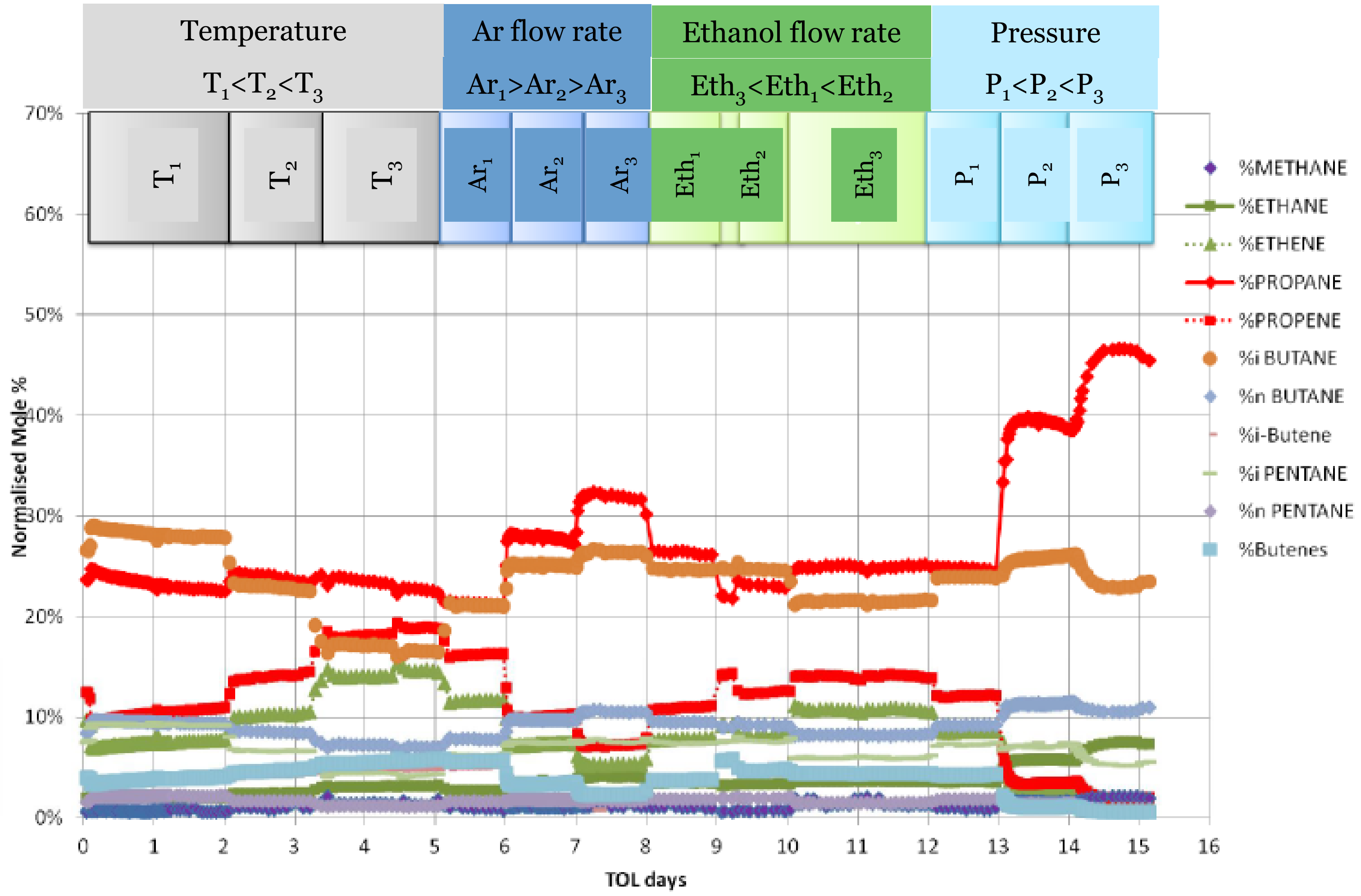
Optimization tests

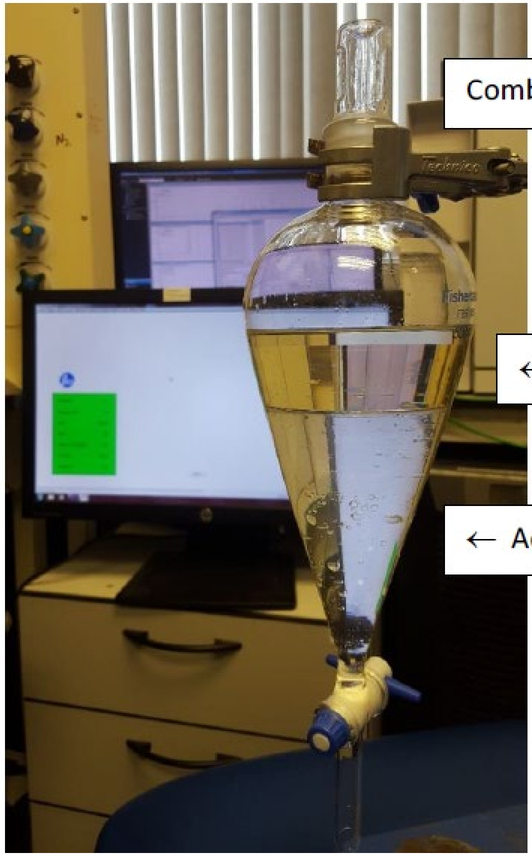
- Different conditions were tested to find the maximum Propane selectivity
- Increasing temperature increased the C_2 & C_3 formation
- Higer pressures increased the alkane formation, especially for C_3
- Lower space velocities increased the Propane formation



Co-products obtained

- In addition to BioLPG, green aromatics and water are obtained
- 2:1 BioLPG selectivity vs green aromatics
- Potential to be a SAF blending compound

C1 - C26 Range	(% wt.)
Paraffins	3.8
Isoparaffins	12.7
Olefins	3.1
Naphthenics	3.7
Aromatics	**76.6**
Unknowns	ND
Oxygenates	0.06



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Collaboration with GTI-Energy: Scale-up phase to TRL 4

GTI ENERGY

- Working with GTI-Energy to scale-up the technology to a 1” reactor

- 2 test campaigns were carried out:

  - 1st Campaign: Catalyst robustness and role of water in catalyst deactivation in a single fixed bed reactor

  - 2nd Campaign: Catalyst regeneration and influence of space velocity in two fixed bed reactors with middle sampling point

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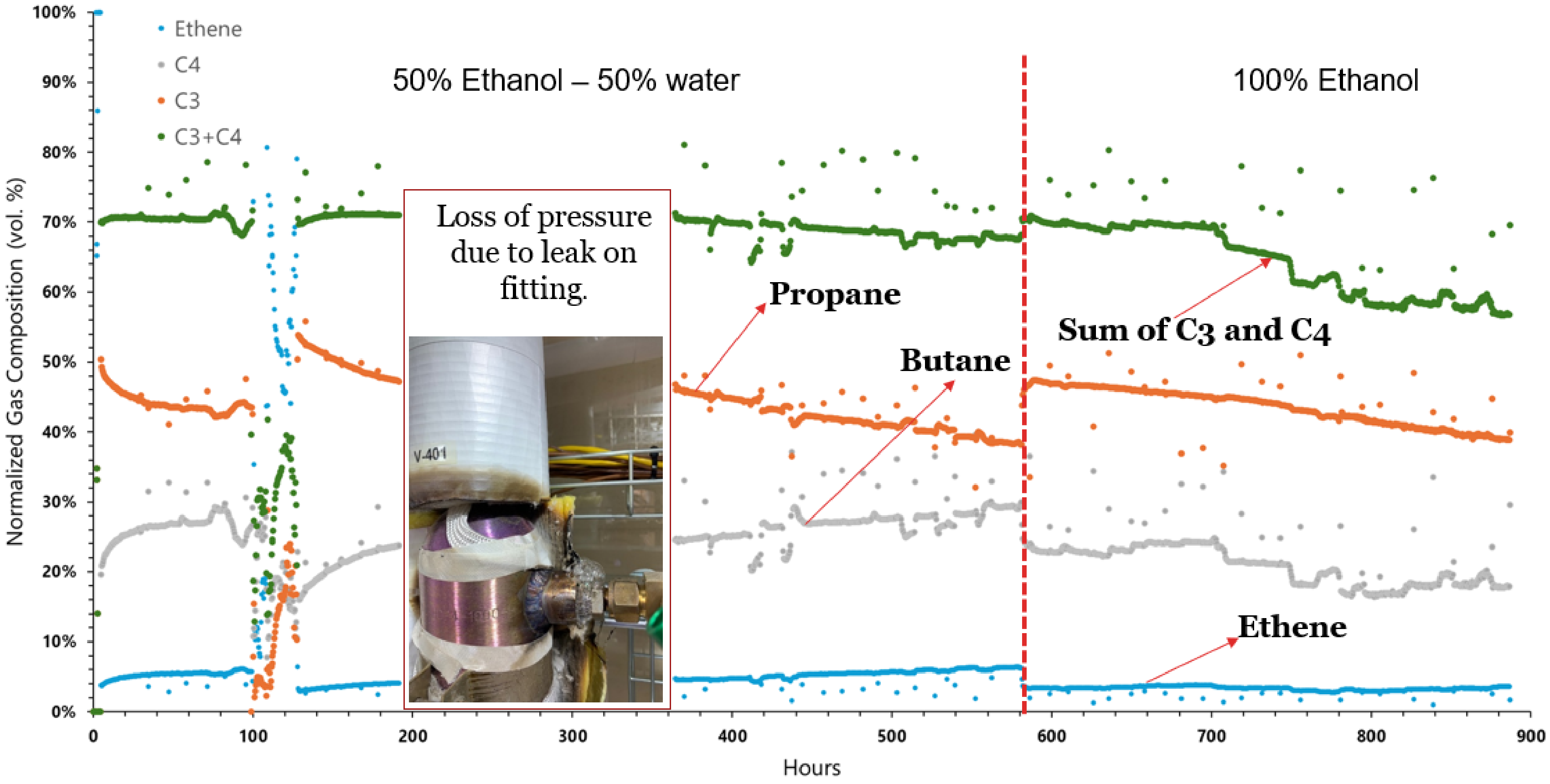
1st test campaign (1 reactor system)

- Catalyst tested for more than 900 hours
- 100% Ethanol run deactivated more severe the catalyst than 50% Ethanol run
- **Middle sample point could have provided more information**



Catalyst stability test with 50% Ethanol – 50% water and 100% Ethanol

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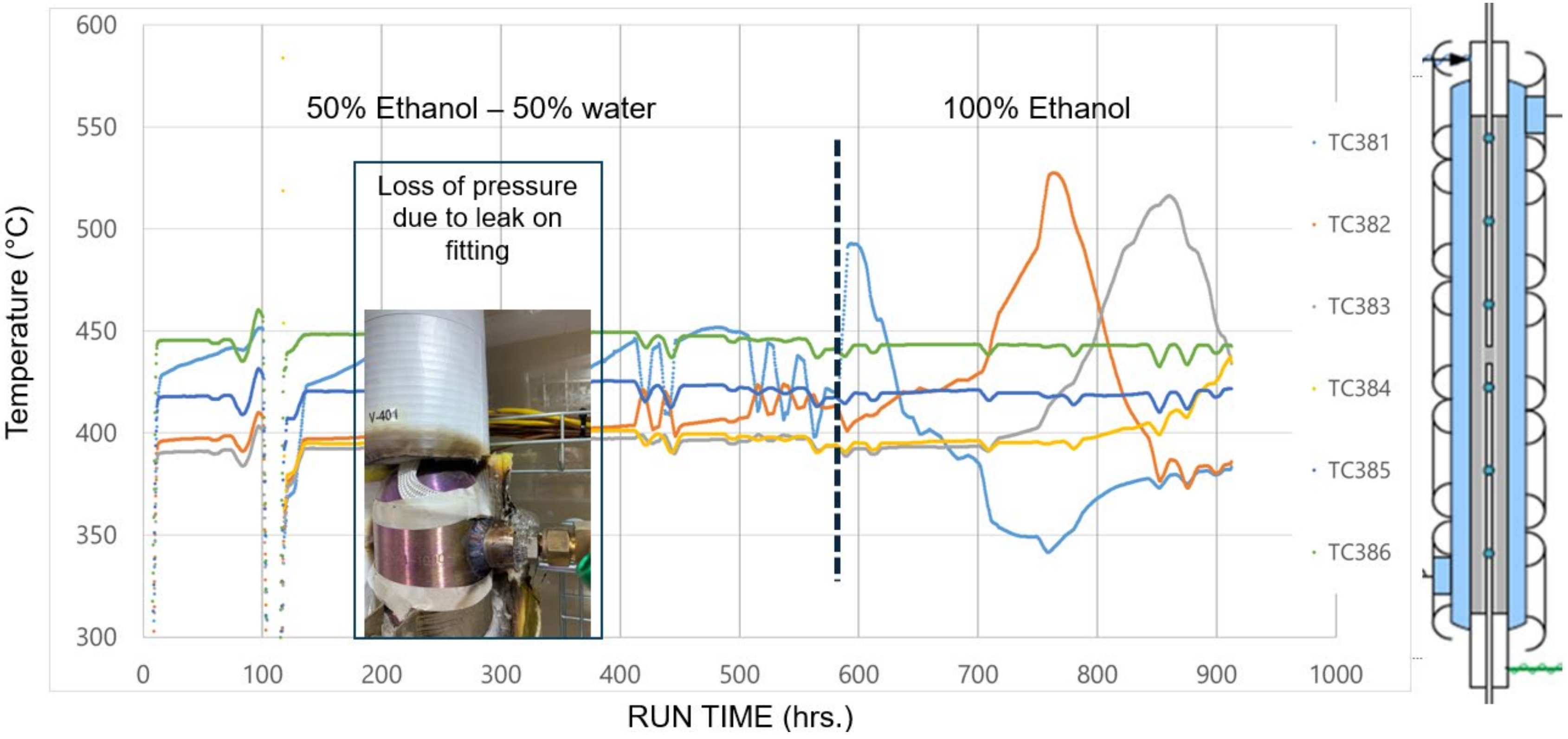

Catalyst stability test with 50% Ethanol – 50% water and 100% Ethanol

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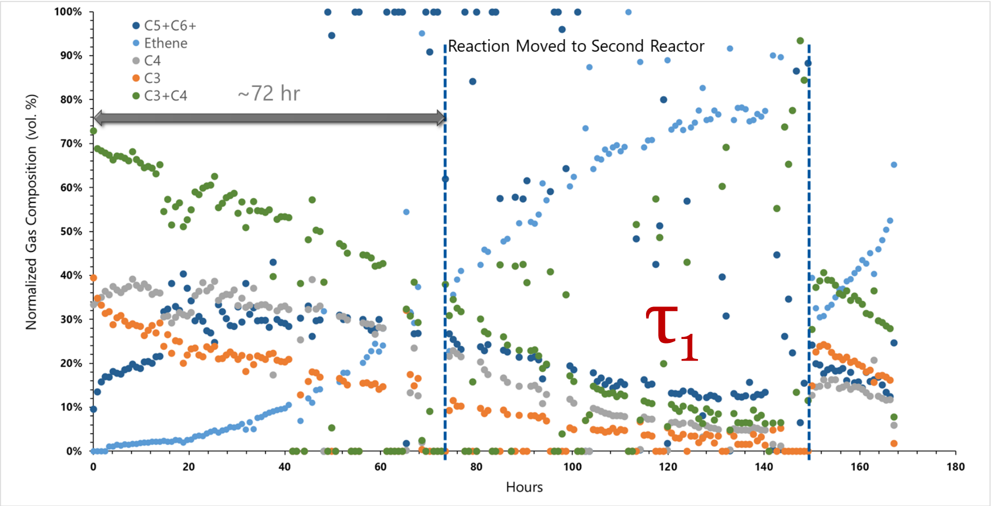
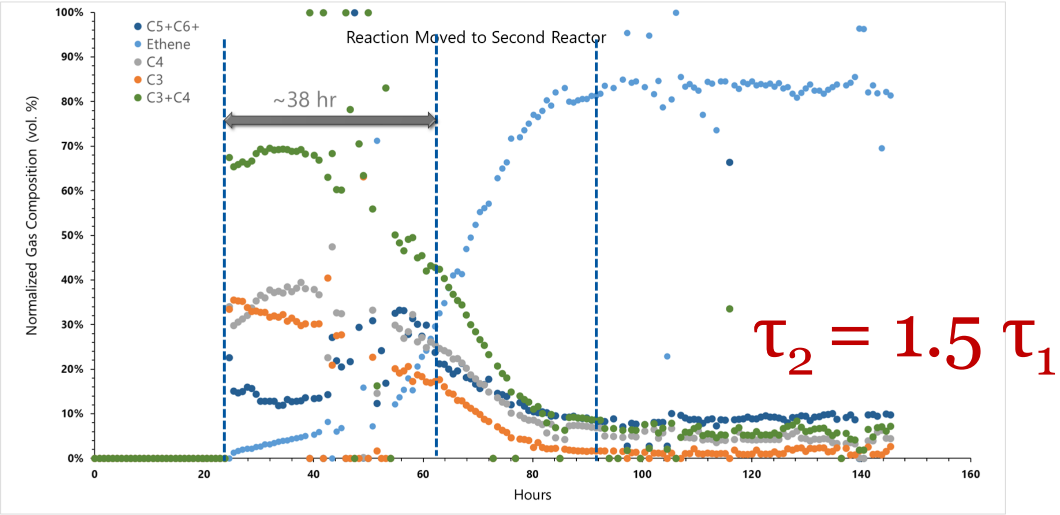
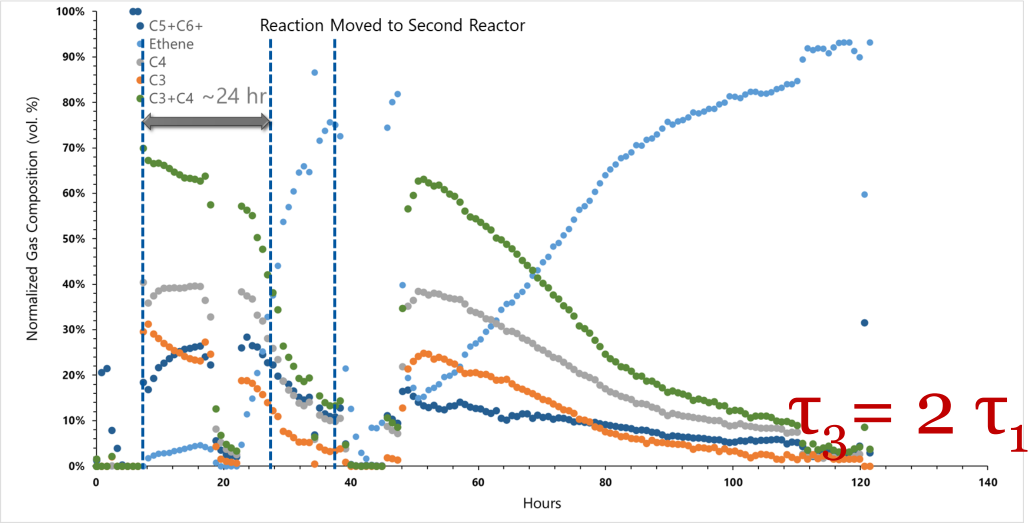
2nd test campaign (2 reactor system)







Variation of space velocity in the 2 reactor system

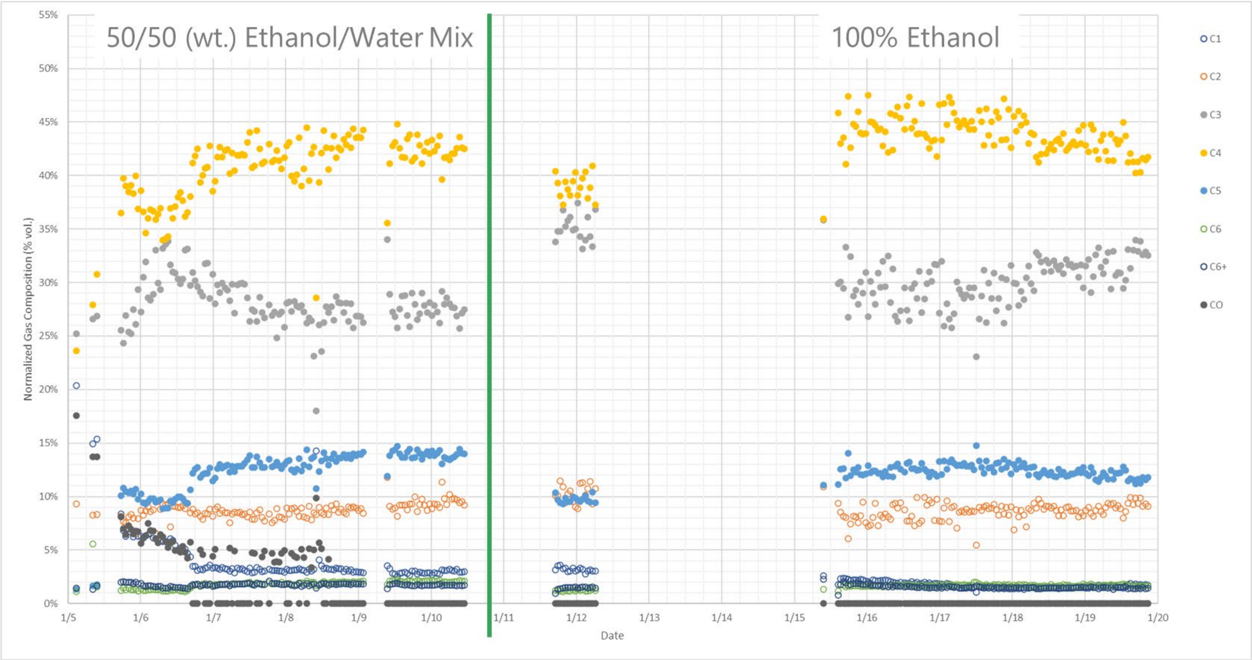
- Reaction front with Ethylene moving at different space velocities
- 2 active sites for the catalyst:
  - Ethanol to Ethylene
  - Ethanol/Ethylene to BioLPG and green aromatics

τ = space velocity

2nd test campaign (2 reactor system)

GTI ENERGY

- Catalyst was regenerated using hot air and tested again with 50% and 100% Ethanol
- More C_4 than C_3 was obtained compared to the fresh catalyst



Performance test of regenerated catalyst with 50% Ethanol – 50% water and 100% Ethanol

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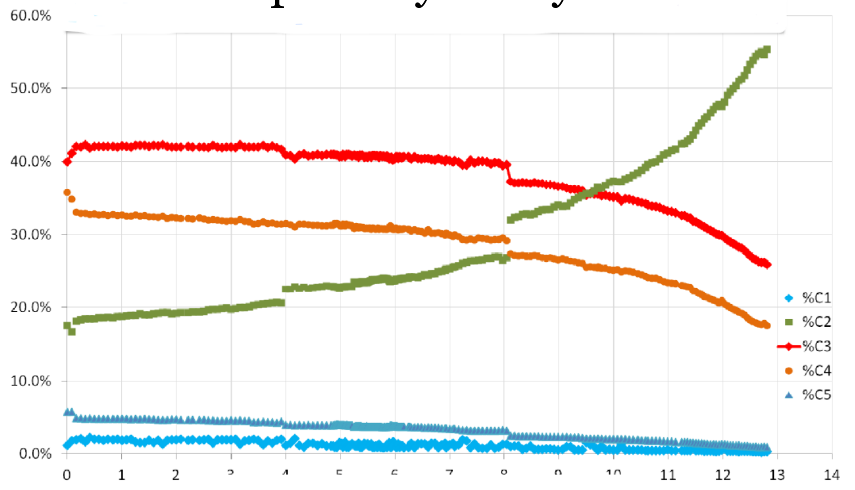
What about testing Ethylene instead of Ethanol with the proprietary catalyst?

- The modified ZSM 5 was used to test Ethylene conversion to LPG at lab scale

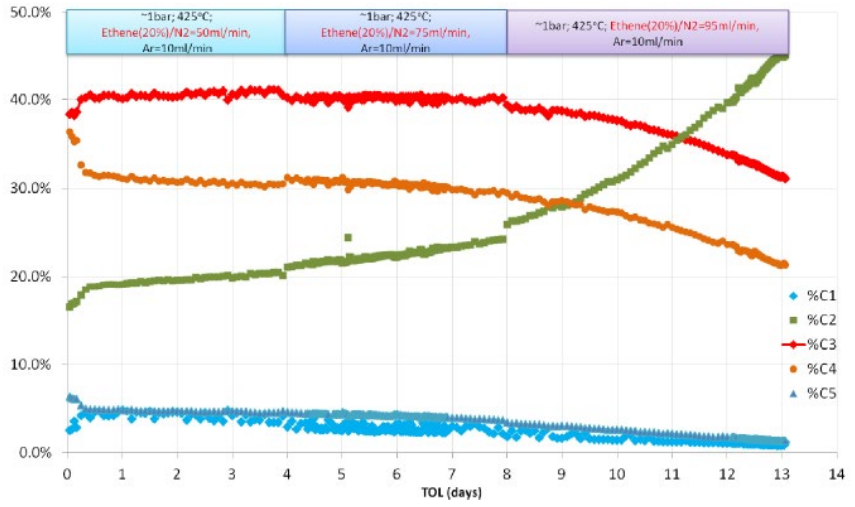
- Ethylene was diluted to 20% using Nitrogen

- The results showed that the catalyst was not stable for more than 8 days, and that there was not much difference with the commercial H-ZSM 5, this means that ethanol plays a key role in the reaction mechanism

Proprietary catalyst



Original H-ZSM 5

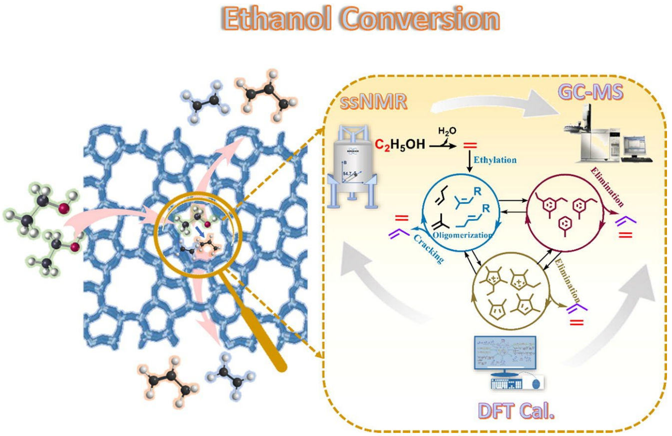


Tests with H-ZSM 5 and modified ZSM 5 with 20% Ethylene

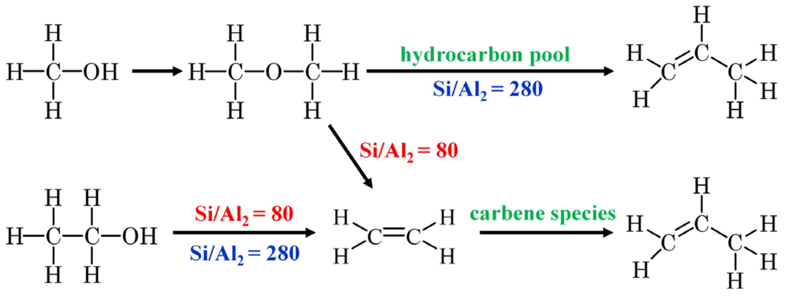
Next step: kinetic model to design the pilot plant reactor

- To be able to scale up the process, a kinetic model is needed. This is a complex system where potentially 2 active sites are involved (Brønsted–Lowry and Lewis acid sites) in the formation of paraffinic C_3 and C_4 and green aromatics

- The challenge is that most of the reaction mechanisms proposed in the literature focus on the formation of alkene, often ignoring the formation of alkanes



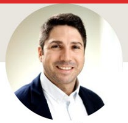
Revealing the roles of hydrocarbon pool mechanism in ethanol-to-hydrocarbons reaction. Journal of Catalysis 413, 517 – 526



Difference between the mechanisms of propylene production from methanol and ethanol over ZSM-5 catalysts. Applied Catalysis A: General 467, 380 – 385.

$$A \xrightarrow{k_1} E$$
$$E \xrightarrow{k_2} O$$
$$E \xrightarrow{k_3} G$$
$$O \xrightarrow{k_4} G$$
$$E \xrightarrow{k_5} P$$
$$G \xrightarrow{k_6} P$$
$$G \xrightarrow{k_7} E + O$$

Kinetic modelling of the transformation of aqueous ethanol into hydrocarbons on a HZSM-5 zeolite. Industrial and Engineering Chemistry Research 40, 3467 – 3474



Miguel Ángel Sánchez García
Lead Chemical Engineer @ SHV Energy |
Engineering Doctorate, Sustainable Fuels |...

T +31 (0) 6511 78273
miguel.sanchez@futuriafuels.com

Thank you!

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