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Conversion of syngas into light olefins in one step for process- intensified production of sustainable aviation fuels

September 2022

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Abstract

Here, we report on a preliminary investigation for direct conversion of syngas into olefins. This technology combines alcohol(s) production and olefin(s) production into a single unit operation to improve process efficiencies due to the overcoming of equilibrium limitations and also to offer capital savings relative to current synthesis approaches including Fischer-Tropsch synthesis, methanol-to-olefins followed by olefins to gasoline/distillate process and alcohol-to-jet process.

Summary

In this study, we investigated the catalytic performance of catalyst mixtures (i.e., alcohol synthesis catalyst mixed with a zeolite-based material) for the direct conversion of syngas into olefins. Operating conditions (i.e., type of catalyst, pressure, temperature and space velocity) were varied to determine the impact on the catalytic performance. While the conversion increases with the pressure and the temperature, the selectivities to products including desired olefins do not vary significantly with changes in pressure (350-450 psig range) and temperature (390-425°C range). The space velocity greatly impacts both conversion and products selectivities. Increasing the space velocity favors the formation of olefins and enables higher olefins/ alkanes ratio but it also results in lower conversion. Overall, this study demonstrates the potential for converting syngas into olefins in one step with limited hydrogenation to alkanes as an olefins/ alkanes ratio above 1 was achieved. However, improvement is still needed to obtain high olefins/ alkanes ratio at high conversion and to limit the water gas shift activity contributing to high CO₂ selectivity.

Acknowledgments

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1.0 Introduction

The global consumption of jet fuel which is equal to ~106 billion gallon/year is expected to double by 2050, potentially resulting in a significant increase of global greenhouse gas (GHG) emissions from the aviation sector. [1] Opportunities for electrification of aircraft appear limited in the near-term due to the low energy density of batteries.[2] Hence, production of sustainable aviation fuel (SAF) has become a prominent strategy for reducing the CO₂ footprint. [3-4] Production of SAF from syngas is a very attractive processing route. First, syngas can be produced from a variety of feedstocks including biomass, municipal solid waste (MSW), and industrial off gasses. Feedstock diversification makes gasification one of the most attractive thermochemical processes for producing biofuels and biochemicals.[1] Additionally, CO₂ can be incorporated into the fuel amplifying further decarbonization. Jet fuel can be made from syngas via three processes 1) Fischer-Tropsch synthesis (FTS), 2) methanol-to-olefins (MTO) followed by olefins to gasoline/distillate (MOGD) and 3) alcohol-to-jet (ATJ). Jet fuel from FTS is limited due to the Anderson-Schulz-Flory distribution reducing the processing carbon efficiency for targeted jet production. Both MTO/ MOGD and ATJ processes enable routes with favorable carbon efficiency, but they have high operating and capitals costs due to multiple unit operations. Direct conversion of syngas into light olefins precursors of jet fuel would eliminate both equilibrium and Anderson-Schulz-Flory distribution limitations while minimizing the number of unit operations.

2.0 Experimental

Reactivity tests for the conversion of syngas to olefins were conducted in a fixed-bed packed bed reactor. A K-type thermocouple was placed in the reactor for measurement of the catalyst bed temperature. To minimize temperature gradients, an electrical resistance heating block was installed for temperature control. Prior to testing, catalysts were first activated *in situ* for 12 hours under N₂. Then, the temperature was cooled down to the desired temperature and the catalysts were exposed to 10% H₂/N₂ for 1 hour prior to reaction. The effects of conversion and selectivity were measured at 390-425°C, 350-450 psig and 1200-5300 GHSV. A knockout pot placed directly downstream of the reaction zone was used to collect liquid product. Gaseous effluent was analyzed online using an Inficon micro-GC (Model 3000A) equipped with MS-5A, Plot U, alumina, and OV-1 columns and a thermal conductivity detector. Liquid samples collected from the knockout pot were analyzed separately *ex situ* using liquid chromatography.

3.0 Results & Discussion

This section reports on the effect of the nature of the alcohol synthesis catalyst and the nature of the zeolite type material on the catalytic performance for direct conversion of syngas to olefins. Effect of operating conditions (i.e., temperature, pressure, and space velocity) were also investigated for one specific catalysts mixture.

3.1 Catalyst screening

Two types of zeolite-based materials labeled at Z1 and Z2 were tested. Experiments were conducted with alcohol synthesis catalyst labeled A3 under the same operating conditions. Table 1 presents the conversion and selectivities to the main products. First, olefins are produced which highlights the potential of the catalysts mixture for producing olefins directly from syngas without complete hydrogenation of the olefins into alkanes. Also, under similar operating conditions the conversion is significantly higher for Z1 (as compared to Z2) and equal to about 27%. This result is surprising since the zeolite material was not expected to impact the conversion of CO. While direct selectivity comparison cannot be conducted at different conversions, one can see that the olefins formation is most desired over Z1. Indeed, over Z1 the olefins/ alkanes ratio is equal to 1.7 but over Z2 the olefins/ alkanes ratio is equal to about 0.8. The metal incorporated into Z2 facilitates undesired hydrogenation of the olefins. Hence, Z1 material was selected for additional experiments where the nature of the alcohol synthesis catalyst was varied.

Table 2. Effect of the nature of the zeolite-based material on the catalytic performance for syngas conversion to olefins.

Zeolite material	conversion	Selectivity (%)			
		Olefins	Alkanes	CO ₂	CH ₄
Z1	27.4	30.3	18.0	42.8	8.5
Z2	<10	15.3	20.1	52.2	<0.1

The catalytic performance of three alcohols synthesis catalyst labeled as A1, A2 and A3 was investigated under similar conditions. For these experiments the alcohol synthesis catalyst was mixed with Z1. The results presented in Figure 1(a) show that under similar reaction conditions (i.e., same temperature, pressure and space velocity), the conversion increases as follows A3< A1<A2. Given that selectivities need to be compared under similar conversion, the space velocity was varied and conversion between 24-36% were obtained. As shown in Figure 1(b), CO₂ selectivity is relatively similar for all catalysts and equal to about 40-50%. Catalyst A2 appears to present high hydrogenation properties since the alkanes selectivity is about twice higher than that of A1 and A3. The CH₄ selectivity is particularly high for A1 catalyst and about 30%. Catalyst A3 presents the highest selectivity toward olefins and was thus chosen for additional testing.

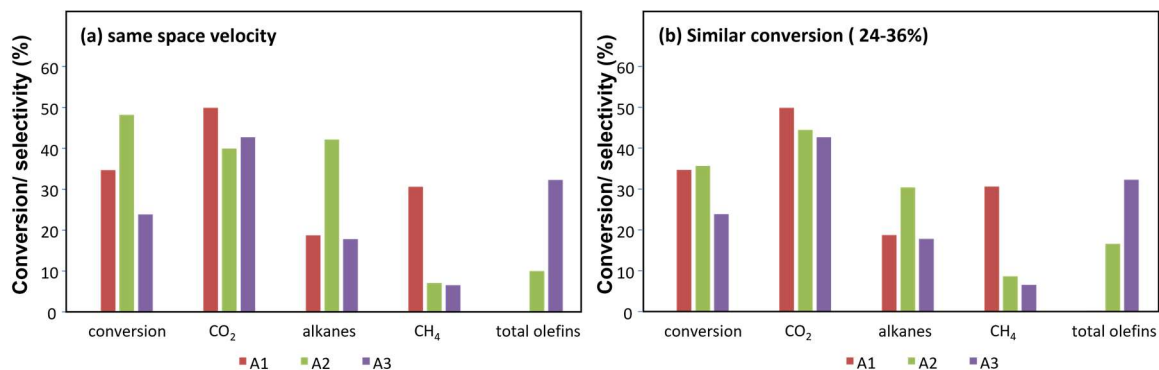


Figure 1. Conversion and selectivities for catalysts A1, A2 and A3 (a) under same operating conditions and (b) under similar conversion.

3.2 Parametric study

3.2.1 Effect of the pressure

Figure 2 presents the catalytic performance of A3 mixed with Z1 over a range of pressures between 350-450 psig. As expected for conversion of syngas into hydrocarbons, the conversion increases with the pressure from 20% (350 psig) to 27% (450 psig). However, the products selectivity remains quite unchanged with the increase of the pressure. The CO₂ selectivity is the highest and equal to about 42% indicating that water gas shift activity is predominant. The desired olefins selectivity is about twice higher than the undesired alkanes selectivity and equal to about 33%. Hence, olefins hydrogenation is relatively limited with this mixture of catalysts.

The pressure has little impact on the product selectivities

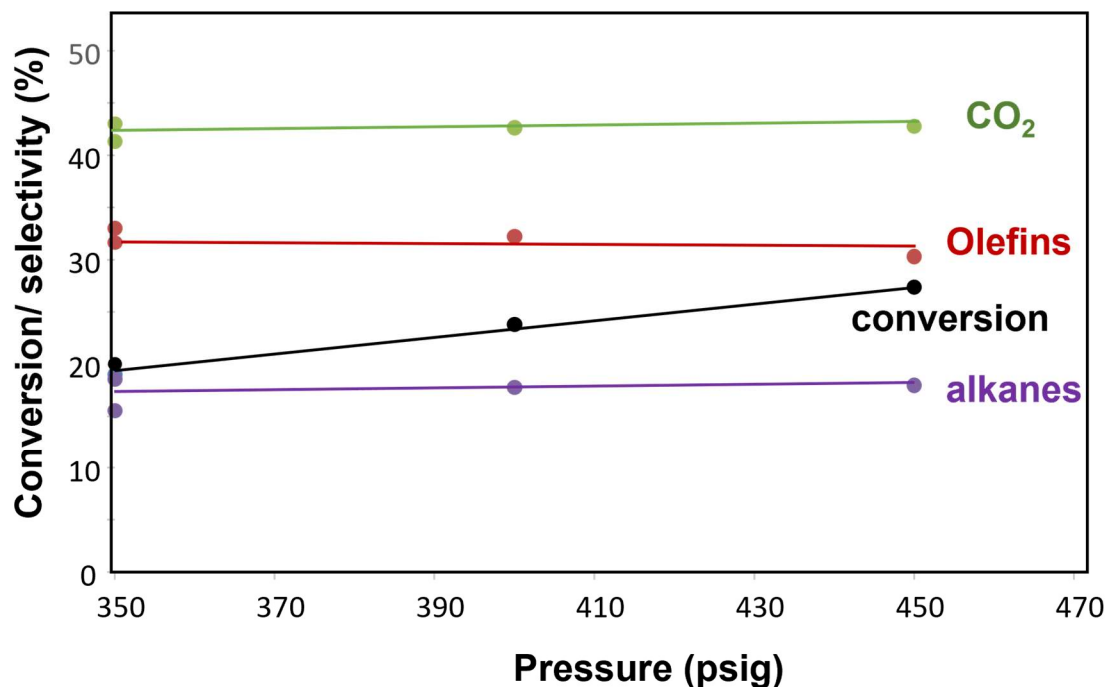


Figure 2. Effect of the pressure on the catalytic performance for A3 mixed with Z1 catalyst mixture.

3.2.2 Effect of the temperature

For the A3+ Z1 catalysts mixture, the catalytic performance was tested at temperatures varied between 390-425°C. The results displayed in Figure 3 show that both conversion and olefins selectivity increase with the reaction temperature. The increase of olefins production with the reaction temperature is accompanied by a decrease in CO₂ formation. For all reaction temperatures tested the olefins/ alkanes ratio is above 1 confirming the limited hydrogenation of olefins to alkanes with the A3+ Z1 catalysts mixture.

The olefins selectivity slightly increases with the temperature from 390 to 410°C

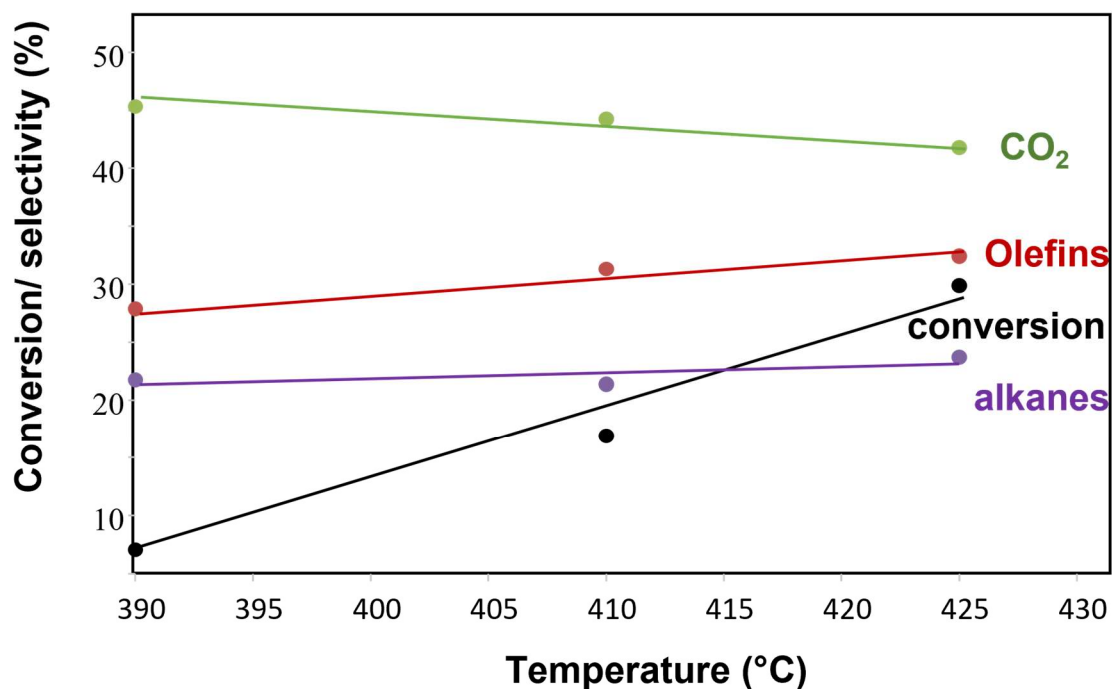


Figure 3. Effect of the temperature on the catalytic performance for direct syngas conversion into olefins over A3 mixed with Z1.

3.2.3 Effect of the gas hour space velocity

The impact of the gas hour space velocity (GHSV) is presented in Figure 4 for the A3+ Z1 catalysts mixture. Both the conversion and the selectivity to alkanes significantly decrease with the increase of the GHSV from 1333 to 5173 hr⁻¹. The decrease of alkanes selectivity with the increase of GHSV is accompanied by an increase in olefins selectivity. The CO₂ selectivity appears less affected by the change in GHSV.

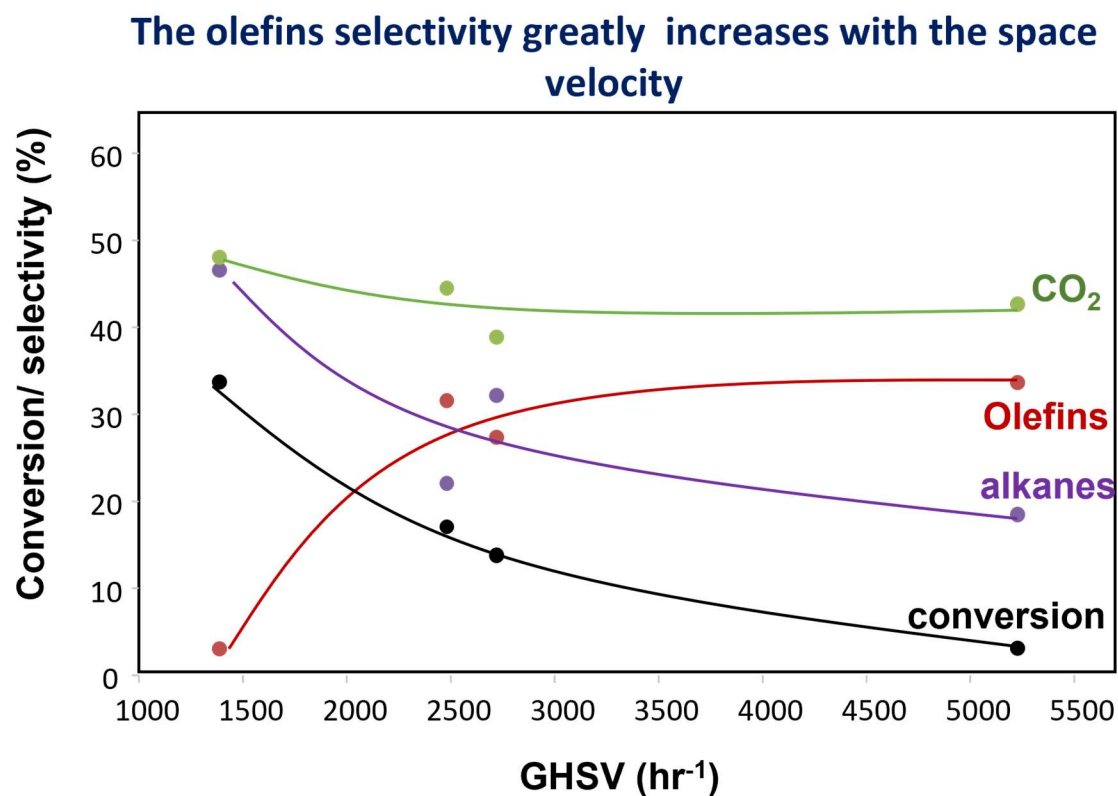


Figure 4. Effect of the gas hour space velocity on the catalytic performance for direct syngas conversion into olefins over A3 mixed with Z1.

4.0 Conclusion

This study demonstrates the potential for converting syngas into olefins in one step with limited hydrogenation to alkanes as olefins/ alkanes ratio above 1 was achieved. However, improvement is still needed to a) obtain high olefins/ alkanes ratio at high conversion and to b) limit the water gas shift activity contributing to high CO₂ selectivity.

5.0 References

- [1] J. Holladay, Z. Abdullah, and J. Heyne, 2020, "Sustainable Aviation Fuel: Review of technical pathways," DOE- EERE. [Online]. Available: <https://www.google.com/search?q=Sustainable+aviation+fuels+review+pathways&rlz=1C1GCEAenUS848US848&og=Sustainable+aviation+fuels+review+pathways&aqs=chrome..69i57j0i22i30.7391j0j15&sourceid=chrome&ie=UTF-8>
- [2] Y. Nakagawa, M. Tamura, and K. Tomishige, "Recent development of production technology of diesel- and jet-fuel-range hydrocarbons from inedible biomass," *Fuel Processing Technology*, vol. 193, pp. 404-422, 2019/10/01/ 2019, doi: <https://doi.org/10.1016/j.fuproc.2019.05.028>.
- [3] Airlines for America, 2020. "Airlines Fly Green." <https://www.airlines.org/airlines-fly-green/>.
- [4] E. S. K. Why, H. C. Ong, H. V. Lee, Y. Y. Gan, W.-H. Chen, and C. T. Chong, "Renewable aviation fuel by advanced hydroprocessing of biomass: Challenges and perspective," *Energy Conversion and Management*, vol. 199, p. 112015, 2019/11/01/ 2019, doi: <https://doi.org/10.1016/j.enconman.2019.112015>.

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