

TRANSFORMING A CRUDE MIXTURE FROM A HYDROFORMYLATION STEP IN CONTINUOUS FLOW WITH A THALESNANO INSTRUMENT SYSTEM TO YIELD VALUABLE FUEL ADDITIVES

INTRODUCTION

With the ever-growing demand for limitless mobility in our world the prospect of sustainable fuels has become a key question for the petrol industry. Major developments in the field of catalysis and process development opened the door for designing tailor-made synthetic fuels, with the possibility of greatly reducing CO₂ emissions^{1,2}.

Featured in this application note, the group of Dr. Andreas Vorholt designed a system for the hydroformylation and continuous flow hydrogenation of olefin-cuts from a Fischer-Tropsch process to achieve bioderived alcohols for a diesel blend with improved characteristics³.

INSTRUMENTATION AND SAFETY CONSIDERATIONS

In the synthetic process developed by the research group a heterogeneous catalytic hydrogenation step was carried out in continuous flow to determine the feasibility of the system for fuel production. The hydrogen gas was generated in situ using an H-Cube® Advance, with the incorporation of the Phoenix Flow Reactor in the flow line, allowing for the extension of parameter scope and scale-up of the catalytic transformation.

Eliminating the risks associated with using hydrogen cylinders in laboratories, the H-Cube® Advance is an all-in-one synthetic platform that utilizes two built-in electrolytic cells to generate hydrogen on-demand from water with up to 60 NmL/min flow rate and 100 bar pressure. The system uses a HPLC pump to carry liquids through the flow line up to 100 bar pressure. With the integrated gas-liquid mixer the instrument creates a uniform mixture from H₂ and the liquid phase.

While the H-Cube® Advance can support 70 mm and 30 mm CatCarts® and perform heterogeneous catalytic reactions from 10°C to 150°C, the Phoenix Flow Reactor, if equipped with metal-metal sealed cartridges (MMS columns), can be used at up to 450°C. The Vorholt group chose to take advantage of the modularity of the instruments by attaching a Phoenix Flow Reactor to the H-Cube® Advance to achieve the extension of temperature and catalyst column scope of their flow system.



With this addition the temperature window of the group's reactor platform was extended up to 450°C and larger MMS catalyst columns could be easily fitted for the possibility of higher throughput reaction optimization. The CatCarts® are designed with ease of use and safety in mind negating the need for direct contact with active catalysts, therefore the pyrophoric nature of the Raney Nickel catalyst does not require any special safety precautions.

Without having to attach a separate back pressure valve at the end of the flow line The H-Cube® Advance's built-in back pressure regulator can conveniently generate and maintain the reaction pressure in the whole system. Operation and monitoring of the H-Cube® Advance - Phoenix Flow Reactor system is done through the built-in touchscreen of the H-Cube®. The integrated pressure sensors before and after the catalyst bed provide useful real-time information on the reaction and system stability. With the addition of a H-Genie® hydrogen generator, coupled with a Phoenix Flow reactor, Pressure Module and Mixer Module, the H₂ generation of the H-Cube® Advance no longer limits the system's throughput capacity, allowing for a possibility of scale-up experiments up to the kilogram/day throughput rate. In this configuration the H-Genie® supplies the reactor with up to 1000 NmL/min 99.99% pure H₂ at 100 bar, without the use of external gas sources.



DISCUSSION AND RESULTS

The Vorholt group's process used a Fischer-Tropsch mixture of various chain-length paraffins and olefins (**1**) as starting material. A hydroformylation study was successfully carried out in a continuously stirred tank reactor setup. The details of this step are presented in the original article³, yielding a mixture of aldehydes **2** and **3**. To achieve the ultimate goal of creating high quality alcohol-based fuel additives **4** and **5**, the crude hydroformylation product mixture was fed directly without any intermediate purification into the ThalesNano continuous flow hydrogenation system (Figure 2) consisting of the H-Cube® Pro and Phoenix Flow Reactor.

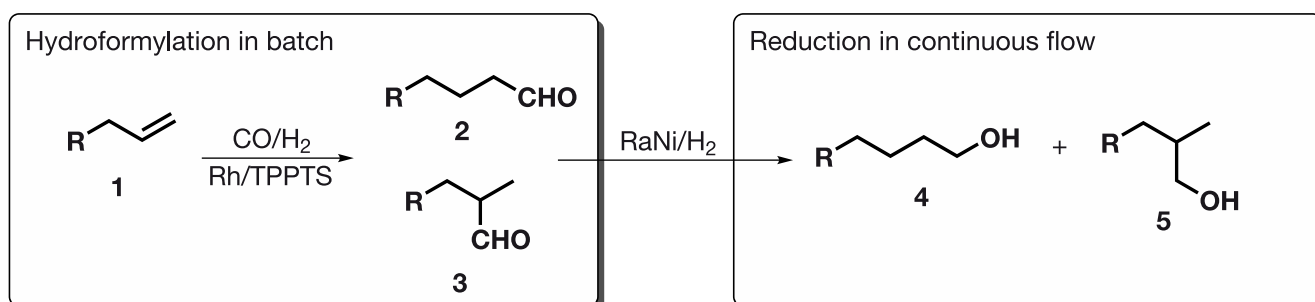


Figure 1: Reaction scheme of Vorholt's experiments

A complete hydrogenation of all C=O and C=C bonds is a requirement to achieve an olefin and aldehyde-free mixture, for this a Raney Nickel CatCart® was utilized. A great indicator of hydrogenation stability and technological robustness is that the same CatCart® was used for over 10 hours in a multitude of experiments. Preliminary experiments at 50°C (WHSV=26.6 h⁻¹) resulted in partial conversion - approximately 60% olefin saturation of leftover alkenes, and 30% aldehyde conversion to the corresponding alcohol were achieved.

Next, the hydrogenation step carried out at 100°C with a slower feed volume of WHSV=13.3 h⁻¹ resulted in quantitative conversion for all carbon chain lengths, with both the olefin and aldehyde conversion soaring above 99%. After a product separation process the desired alcohol mixture with a great potential of being used as fuel additives could be achieved⁴.

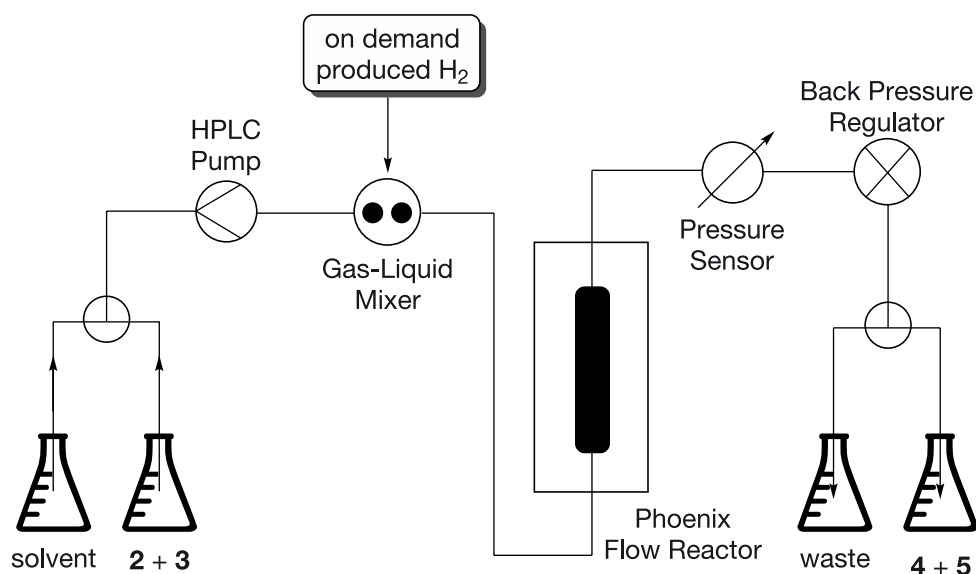


Figure 2: Platform setup for the continuous flow hydrogenation of the aldehydes **2** and **3**

SUMMARY AND CONCLUSIONS

The Vorholt group's work presented great insight for chemists and engineers working on process development in the field of alcohol-based fuel additives. The group's results show the capabilities and feasibility of integrating ThalesNano instruments in petrochemical process development and the benefits of continuous flow chemistry with regards to optimization, scalability and enhanced reaction rates.



REFERENCES

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