APPLYING CONTINUOUS FLOW TECHNOLOGIES FOR THE VALORISATION OF LOW-COST RAW MATERIALS INTO USEFUL PETROCHEMICALS, FUELS AND API'S

INTRODUCTION

In our days the importance of developing sustainable and green processes is one of the pivotal points in chemistry and chemical engineering. The benefits of continuous flow technologies broaden the horizons of chemists working in the ever-growing fields of research and industry. In this application note we feature the work of Carlos Afonso's group centered around furfural - an entry in the U.S. Department of Energy top "10+4" list of bio-based materials[1,2], as well as the work of Prof. Dr. Jeroen Anton van Bokhoven's group on the benefits of H_2 in reductive catalyst reactivation and converting carbonaceous deposits into hydrocarbons of high value[3].

INSTRUMENTATION AND RISK ASSESSMENT

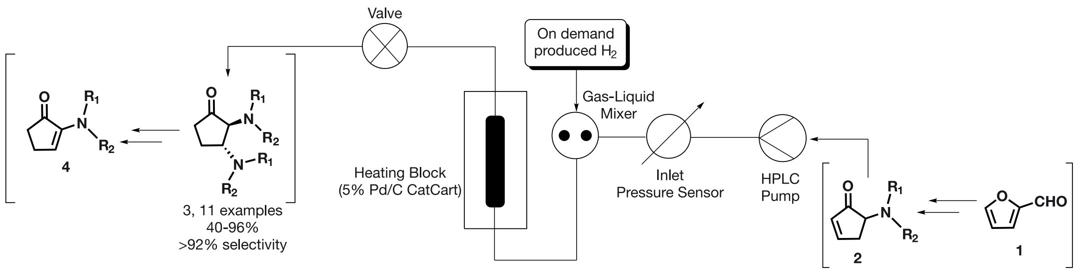
To overcome the need for intermediate isolation and purification steps during the synthesis of α-enaminones directly from furfural the Afonso group coupled their continuous flow system[4] with the H-Cube® Mini Plus in a sequential configuration. While the H-Cube® Mini Plus is an easy to learn, all in one flow chemistry platform that offers in-situ on-demand hydrogen generation using water electrolysis, given the typical scale of reactions in applications for the fuel industry a reactor configuration featuring the Phoenix II Flow Reactor and the H-Genie® 2.0 Hydrogen Generator could be of consideration for chemists in these fields. Eliminating the risks associated with the use of H_2 cylinders in the laboratory, the H-Genie® 2.0 is a capable of supplying a scale-up synthetic platform with hydrogen generated from deionized water with gas flow rates up to 1 NL/min and 100 bar pressure. Reaction optimization and parameter screening can just as easily be carried out in the Phoenix II as in the H-Cube® Mini Plus, with the addition of a wider parameter scope allowed by greater temperature and pressure tolerances of the reactor module. Using a wide range of user-fillable metal-metal sealed catalyst columns in the reactor the maximum heating capabilities of up to 450 °C can be utilised. A highly modular reactor configuration gives chemists the ability to design synthetic platforms for safe and convenient reaction scaling in the gram-kilogram range. Pre-packed and closed catalyst cartridges (CatCarts®) can be seamlessly utilised in the Phoenix II Flow Reactor minimising the exposure of the user to the active catalysts and eliminating catalyst filtration. In a scale up system the Pressure Module is responsible for building the reaction pressure up to 200 bar to avoid overboiling of solvents carried by HPLC pumps with the capacity of 10 ml/min or 50 ml/min.

Bokhoven's group designed a special flow reactor using multiple Gas Modules to achieve accurate and reproducible gas dosing during catalyst studies. Allowed by a built-in Mass Flow Controller (MFC) the Gas Module is capable of accurately regulating the flow of 13 different gases and gas mixtures with up to 100 NmL/min flow rate and maximum outlet pressure of 135 bar. The Gas Module Plus broadens the parameter scope of experiments with up to 1000 NmL/min maximum flow rate, allowing for extended scale-up capabilities. Seamlessly integrating with other ThalesNano instruments the Gas Module enables the creation of highly modular reactor fleet configurations. Connected to multiple ThalesNano instruments, as the Phoenix II. Flow Reactor, H-Genie® 2.0, THS System Controller®, Pressure Module, the Gas Module benefits from fleet-wide automated safety features and automation capabilities. In stand-alone mode, pressing the emergency stop button will safely and immediately stop the flow of gases and close the valves inside the unit.

DISCUSSION

Tunable Continuous flow hydrogenation of bio-based cyclopentenones[1]

In a recent paper published in RSC Reaction Chemistry & Engineering the Afonso group used furfural (**1**) for developing a multi-step continuous flow technique for the selective synthesis of novel cyclopentenones (**4**) (Scheme 1), a highly relevant intermediate for pharmaceutically cardinal compounds5. Previous batch experiments used a large excess of oxidants and had limitations in physical parameters. The groups' continuous flow protocol successfully eliminated both issues, resulting in great yields and selectivities in 11 examples in the synthesis of **3**[1].



Scheme 1: Multi-step continuous flow process for the synthesis of novel cyclopentenones **4**

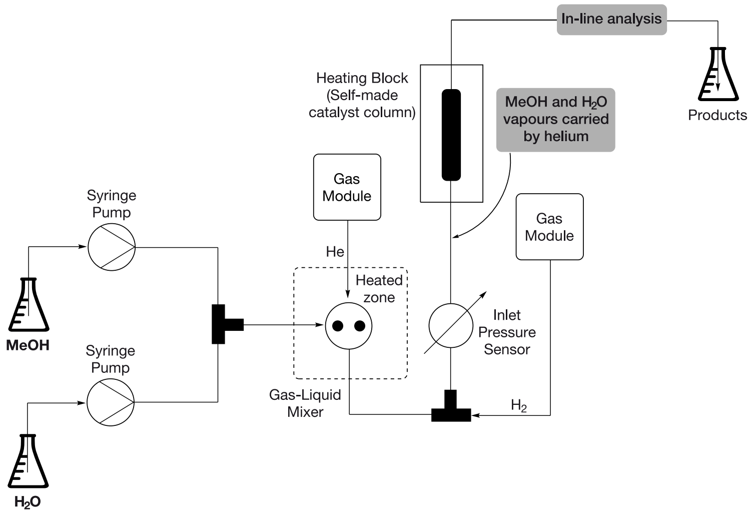
The high catalyst to substrate ratio and quicker reaction times achieved by this technique facilitate better selectivity coupled with the inherent improvement of reaction safety by small reactor volumes. Catalyst and parameter screening of the continuous flow hydrogenation of diamino-cyclopentenones was carried out in the H-Cube® Mini Plus.

Optimization experiments showed that 5% Pd/C, 20% Pd(OH)2/C, and 10% Pd/Al_2O_3 CatCarts® allowed to run more than 40 reactions, tolerated various substrates without the loss of efficiency and without cross-contamination. 5% Pd/C proved to be the most effective in terms of yields (up to 96%) and selectivity (>92%). Optimal conditions turned out to be room temperature and 10 bar of reaction pressure, with a flow rate of 0.5 mL/min of a 0.035 M ethanolic solution of **2**. In a subsequent reaction step, the base promoted elimination of an amino group yielded the desired **4** in a single, cascading flow reactor setup[1].

Reactivation of catalysts for methanol-to-hydrocarbons conversion with hydrogen[3]

Besides furfural, another technology of high importance in the fuel industry is the conversion of methanol to hydrocarbons (MTH) of various chain lengths. However, the formation of "coke" – solid carbonaceous deposits with complex composition – on catalyst surfaces is a well-known technological difficulty. In Bokhoven's work, researchers have integrated a set of Gas Modules from ThalesNano into their continuous flow setup, achieving the reduction of coke deposits from their catalysts (Scheme 2)[3].

To study catalyst regeneration, catalytic testing was carried out in two phases. ZSM-5 zeolite catalysts with varying Al content, mixed with SiC were loaded into a stainless-steel reactor with the internal diameter of 5 mm. Various levels of catalyst deactivation were purposely induced by methanol-to-hydrocarbon reactions in continuous flow using 400 °C and 1.5 bar. In the second phase, the deactivated catalysts were subjected to hydrogen treatment with H_2 flow of 100 NmL/min at 480 °C or 550 °C and 20 bar.



Scheme 2: Continuous flow process for the study of deactivation and reactivation of zeolite MTH catalysts

To determine reaction parameters the reactor inlet and outlet were analysed by MS, GC-FID and GC-MS. In the case of ZSM-5 ($Z_{15}M_mH_m$, Si/Al atomic ratio: 1:4) substantial catalyst reactivation was achieved at 20 bar pressure, with conversion of 82%. Raising the time of treatment from 0.85 h to 5 h and temperature to 550 °C resulted in substantial improvement of turnovers. Detailed physical-chemistry and NMR results and further observations are featured in the original article[3]. In the case of zeolites with higher Al content the H_2 treatment proves to be particularly effective with the removal of up to 96% of coke deposits. Products such as methane, ethane, alkylated benzenes and naphtalenes prove the high potential of converting undesirable coke deposits into highly valuable hydrocarbons to be used in the petrol industry.

SUMMARY AND CONCLUSIONS

The two papers featured in this application note shed light on the importance of continuous flow processes in the field of bio-based materials and the fuel industry. From rapid parameter and catalyst screening, enhanced productivity, to the ease of use, easy implementation, inherent safety features of flow chemistry and ThalesNano's equipment these two excellent examples of research provide great insight for all who's interested in the field of fuels and green chemistry.

REFERENCES

1. Lídia A. S. Cavaca, Carlos A. M. Afonso et al., *React. Chem. Eng.*, **2023**, 8, 482.
2. Joseph J. Bozell, Gene R. Petersen, *Green Chem.*, **2010**,12, 539-554.
3. Vladimir Paunovic, Jeroen A. van Bokhoven et al., *Journal of Catalysis*, **2022**, 407, 54–64.
4. Rafael F. A. Gomes, Carlos A. M. Afonso et al., *Sustainable Chem. Eng.*, **2021**, 9, 16038–16043.

5. a. Vincenzo Calderone, Violetta Cecchetti et al., *J. Med. Chem.* **2008**, 51, 16, 5085–5092.

5. b. Alma Martelli Violetta Cecchetti et al., *J. Med. Chem.* **2013**, 56, 11, 4718–4728.

For more information, please visit
www.thalesnano.com
linkedin.com/company/thalesnano-inc-/
twitter.com/thales_nano
instagram.com/thalesnano_inc/
facebook.com/ThalesNano/

ThalesNano Inc.
Záhony utca 7. | H-1031 Budapest | Hungary
Phone: +36 1 880 8500
Fax: +36 1 880 8501
Email: sales@thalesnano.com
www.thalesnano.com

US Office
50 S. Penn St. Suite B-2
Hatboro PA. 19040
USA
Phone: 215-534-3365
E-mail: USAsales@thalesnano.com