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TNO report

TNO 2021 R10510 | Final report

Black Birds (TEBE 117010) Public Final Report

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Summary

“Black Birds - Combined thermochemical and catalytic processing adapted for the production of high-value products and energy from lignin” is a TKI project financed by RVO (reference TEBE 117010) that applies the “adaptive radiation” concept to the valorisation of lignin from different biorefinery processes into a portfolio of products with different niche applications. This includes the use of lignin in a combustion process or in the gasification with co-production technologies leading to bio-BTX, bio-ethylene and bio-SNG.

Lignin Y and lignin A were tested under realistic pulverised fuel combustion conditions in the LCS (lab-scale combustion simulator) at TNO. It could be demonstrated that neither significant near-burner slagging nor excessive heat exchanger fouling can be expected from the outcome of the tests. However, in a co-firing scenario with a fuel that contains cations that can react with the chlorine present in the lignin, chloride salt formation is likely to happen which can cause (alkali-) salt induced heat exchanger fouling and potentially high temperature chlorine corrosion. Nitrous oxide formation is not expected to be problematic, provided minimum burner air staging is applied. From an operational point of view, potential corrosion issues appear to form the highest risk when firing lignin A.

The gasification of lignin A in the 5 kW_{th} WOB bubbling fluidized bed gasifier leads to lower amounts of product gas (and as consequence larger amounts of char) though it also leads to similar values of ethylene, benzene and toluene as compared to beechwood gasification (reference material). Gasification at 850°C is preferred over 780°C since it leads to a substantial increase of benzene, toluene and ethylene. Also measures to improve char gasification reactions such as an increase of steam as carrier gas should be taken.

The selective adsorption of ethylene from the product gas was the subject of the study performed by Avantium. Combinations of different zeolites and active carbons were made in order to tune selectivity. In order to enhance ethylene sorption selectivity, different sorbents were combined in layered or mixed beds. It was concluded that Zeolite [Ca]A and carbon GCN-3017 or combinations of these materials are the best options for ethylene adsorption from the product gas .

In a review performed by Catalok, Zn was identified as a potential substitute of Ga in the conversion of ethylene into aromatics. However with the parametric study commissioned to the University of Ghent it was concluded that Ga-ZSM-5 (0.2 wt% Ga) is a better candidate for the aromatics (BTX) production from C_2H_4 as compared to Zn-ZSM-5 (0.1 wt% Zn) due to its selectivity (up to 16%) and stability. Increasing total pressure leads to a lower conversion of the C_2H_4 which is attributed to fast carbon formation. However, the catalysts can be regenerated by air without loss of initial activity.

The BTX scrubber unit (AREA) was modelled using the Aspen simulation tool, which showed that several parameters could be optimized without significant loss of efficiency. Based on this several experiments were performed and the following could be achieved:

- The L/G ratio could be lowered from ~33 kg/Nm^3 to ~11 kg/Nm^3 maintaining 97% benzene capture.
- Steam was lowered from 820 g/h (stripper L/G~24) to 410 g/h maintaining 97% benzene capture.

AREA was upscaled to be able to process the full product gas generated in the MILENA gasifier about 5 Nm^3/h. The past experiments were performed on a slip stream of about 1 Nm^3/h of product gas. The operating conditions chosen for the demonstration tests were based on the optimization work:

- Absorber temperature: 35°C
- Stripper temperature: 130°C
- Oil circulation: 50 kg/h
- Stripper steam: 2 kg/h

The demonstration tests were conducted successfully at the 25 kW$_{th}$ MILENA reactor and proved the feasibility of the co-production technologies developed with the Black Birds project. The first demonstration test (Configuration 1) successfully co-produced bio-BTX and bio-SNG with ethylene aromatization via gasification of lignin. Bio-BTX was selectively removed from the product gas with 98% efficiency. The analysis of the collected sample shows about 85% on mass basis of benzene, toluene and xylenes. However, the activity of the catalyst used in the ethylene aromatization unit (DEA) was lower than expected and mainly toluene was formed. The second demonstration test (Configuration 2) successfully removed ethylene and carbon dioxide selectively from the product gas. However the sorbent reach saturation after about 15 minutes.

The application development of the bio-BTX, coordinated by Viride, was performed in close collaboration with end-users. Two different applications were identified for the bio-BTX product:

- Use it directly as collected in the aromatics train
- Purify the benzene for detergent production

A Techno-Economic Evaluation was performed as part of a PDEng final year assignment from the TU Eindhoven. Some of the main findings can be summarized as follow:

- At market prices the co-production of bio-BTX improves the revenues of the SNG production by 30 % for scenario 2 (SNG with co-production of BTX) and 60% for scenario 3 (SNG with co-production of BTX via ethylene aromatization)
- At fossil based market prices, the business case of all scenarios is negative
- CO$_2$ values of 150 €/kg provide an ROI of 10% for scenario 3.

This public report summarizes the main achievements of the project.

Project reference number	TEBE 117010
Project title	Black Birds: Combined thermochemical and catalytic processing adapted for the production of high-value products and energy from lignin
Project partners	TNO (Coordinator), Avantium, Catalok, Kodok, Viride
Project duration	01-01-2018 / 31-12-2020

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1 Introduction

The Dutch government aims with the National Climate Agreement to reduce greenhouse gas emissions in the Netherlands by 49% by 2030 compared to the 1990 levels. Hereby an integral knowledge and innovation agenda (IKIA) is established where five "missions" are defined containing 13 MMIPs (multi-year mission driven innovation programs). Integrated in Mission C the role of biomass is defined, and it is expected that by 2030 biobased feedstocks are fully implemented and considered to be "standard" [1]. One option of achieving this is by the use of cheap waste as biomass source and by the co-production of green chemicals while generating green energy from biomass. The "Black Birds" project will contribute to this objective by valorising lignin from a 2nd generation biorefinery into a range of products with different niche applications.

The "Black Birds" project applies the "adaptive radiation" concept to the valorisation of lignin from different biorefinery processes into a portfolio of products with different niche applications. The gasification of new bio-based feedstocks could require new feeding methods and result in different compositions of the producer gas. The sorption technology developed in the previous "Green Birds (TEBE113008)" and "Blue Bird" (TEBE115001) projects was adapted to be applied in different phases of upgrading the producer gas. Finally, this innovation project takes a step forward in the implementation of co-production of chemicals applied to bio-SNG production by upscaling some of the novel co-production technologies in preparation of pilot scale test.

The research plan was applied to 4 main areas:

1. Valorisation of lignin side-stream from Avantium's novel DAWN process through thermochemical conversion (gasification and/or combustion) into heat/power, fuels and green chemicals.
2. Further optimization and fine-tuning of the catalytic conversion (ethylene aromatization) and chemical absorption/adsorption technologies developed by TNO and Avantium for the production and harvesting of aromatics (bio-BTX), ethylene (C_2H_4) and the upgrading of gasification product gas.
3. Upscaling of the technologies up to ~ 5 Nm^3/h feed gas. The upscaling includes the application of sorbents and catalysts using industrially relevant procedures.
4. Study of suitable applications of the bio-BTX product, with focus on the production of polymers.

The implementation of these new technologies for the recovery of high-value compounds from gas will eventually result in an overall decrease of the production cost of bio-SNG by simultaneous tackling 2 factors: use and valorisation of a low-cost by-product (in this case, lignin from biorefinery processes) and increase of the value of the bio-SNG process by the harvesting of ethylene (catalytically converted into aromatics) and the subsequent recovery of the bio-aromatics co-product. Catalytic conversion of ethylene into BTX generates a liquid product, thus overcoming the logistics of ethylene (gas) transport while keeping the value as aromatics. Figure 1.1 shows the "Black Birds" schematic concept. The research and demonstration tasks

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[1] "Climate Agreement", The Hague, 28 June 2019 (National Climate Agreement - The Netherlands | Publicatie | Klimaatakkoord)

are complemented by a cross-cutting techno-economic and market analysis of the overall process.

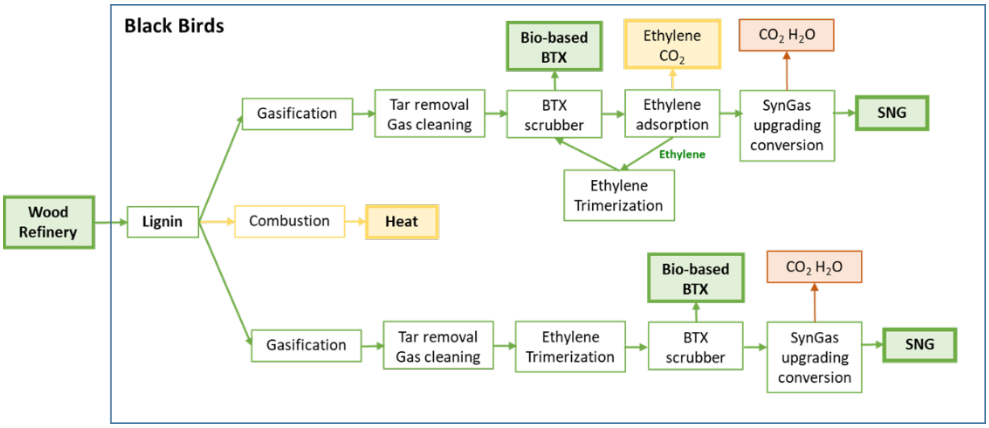

Figure 1.1 “Black Birds” schematic concept

1.1 Project Overview

Project reference number	TEBE 117010
Project title	Black Birds: Combined thermochemical and catalytic processing adapted for the production of high-value products and energy from lignin
Project partners	TNO (Coordinator), Avantium, Catalok, Kodok, Viride
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In order to fulfil this objective, a strong consortium that covers the whole value chain has been formed: Avantium brings its research resources and extensive know-how in catalysts and sorbents, while also supplying the lignin feedstock from their pilot plant. TNO contributed with the experimental facilities and expertise in thermochemical and catalytic processes (pyrolysis, gasification, combustion, bio-SNG production). Kodok used its capabilities in market analysis of bio-products. Catalok, with its large expertise in catalytic process, played an important advisory role in ethylene aromatization. Viride supplied the lignin benchmark samples and coordinated the involvement of BTX end users who brought their vision of bio-aromatics production and commercialization to the market analysis and TEE activities. In close cooperation with the end-users, the BTX samples produced in the project were tested against market specs and initial test products were made for validation and as demonstration of this new technology.

1.2 Structure of the report

Chapter 2 shows the main findings on characterization and thermochemical valorization of several lignin samples performed at TNO. Chapter 3 describes the work on sorbents realized at Avantium. Chapter 4 is devoted to the ethylene aromatization work and presents the work performed by Catalok and the work commissioned to the University of Ghent. Chapter 5 describes the work on AREA

(Aromatics REcovery Apparatus) for BTX removal and its upgrade at TNO. Chapter 6 shows the demonstration study of the technologies at the larger scale 25 kW_{th} at TNO. Chapter 7, coordinated by Viride, focus on the developments in the application of the bio-BTX and on the logistics of the overall process performed by Kodok. Finally chapter 8 presents the Techno-Economic Assessment (TEE), performed by a PDEng as part of his last year assignment. Chapter 9 summarizes the conclusions and outlook of the project.

2 Thermochemical Valorisation of Lignin

This chapter is devoted to the experimental work performed at TNO with respect to the thermochemical valorisation of lignin as a side stream from a 2nd generation biorefinery. This work was carried out on a step approach:

1. Lignin characterization
2. Combustion tests
3. Gasification tests at small scale
4. Feasibility tests (Chapter 6)

2.1 Lignin characterization

Several samples of lignin supplied by Viride and Avantium were characterized at TNO. These samples were produced from different biomass sources and at different conditions. Table 2.1 shows the proximate and ultimate analyses of the received samples.

Table 2.1 Proximate and ultimate analyses of the received lignin samples

Lignin Samples		*Y*	*A*	*B*	*C*	*D*
Br	mg/kg	< 10	32	< 10	< 10	< 10
Cl	mg/kg	10446	15990	198	185	182
F	mg/kg	< 10	< 10	513	38	14
S	mg/kg	-	558	794	858	1028
Ash content (550°C)	% db	0.1	1.0	16.9	3.0	2.8
Volatile matter	% db	68.4	64.3	64.6	79.0	79.6
Moisture content	% ar	2.9	5.1	4.5	3.8	2.9
HHV	MJ/kg	23.2	24.8	18.1	20.7	21.5
C	% db	57.2	60.1	43.5	50.4	52.0
N	% db	0.2	0.5	0.7	1.0	1.1
H	% db	5.8	5.6	5.0	6.2	6.3
O	% db	33.6	30.1	33.6	39.6	38.0

The lignin samples C and D are very similar and are the ones with the highest volatile matter but also with the largest amount of oxygen. These samples are obtained from the same feedstock but are subjected to a different conditioning. Lignin A has a small amount of ash, less than all the other samples, and has more carbon content, which leads to a higher energy value (HHV). However it is also the sample with the largest amount of chloride, which is almost meaningless in all other lignin samples with the exception of lignin Y. This is of some concern due to the possibility of salt formation and corrosion during the thermochemical processes. Lignin B and lignin X have the largest amount of ash and the lowest amount of carbon. As consequence they are also the samples with the lowest energy value.

2.2 Lab-scale Combustor Simulator (LCS) tests

The TNO lab-scale combustion simulator (LCS) is a flexible facility for the characterisation of solid fuel behaviour under typical pulverised fuel fired furnace and gasifier conditions. The facility comprises a drop tube reactor together with a primary/secondary gas burner to simulate a flame/flue/syngas environment in which the conversion behaviour of fuel particles can be studied as function of time. An adequate simulation of heating rate, gas temperatures and composition can thus be obtained independently of the test fuel. The approach is specifically suited to study secondary fuels under primary fuel conditions. An impression of the LCS rig is presented in Figure 2.1.

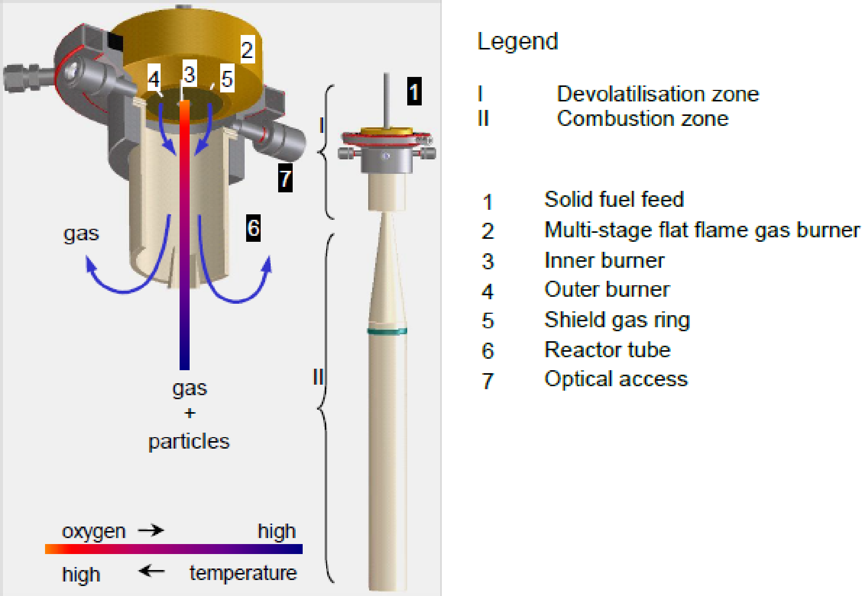


Figure 2.1 Staged flat flame gas burner and reactor (drop) tube in TNO combustion simulator

2.2.1 Slagging and Fouling

The ash formation and deposition on the refractory and the heat exchanging surfaces of the boiler (slagging and fouling phenomena) are one of the most common causes of maintenance requirements at coal-fired power plants. Near burner slagging tests were performed using the vertical deposition probe, shown in Figure 2.2. Different coupons can be attached to the probe head to simulate different deposition surfaces in terms of material and surface structure.

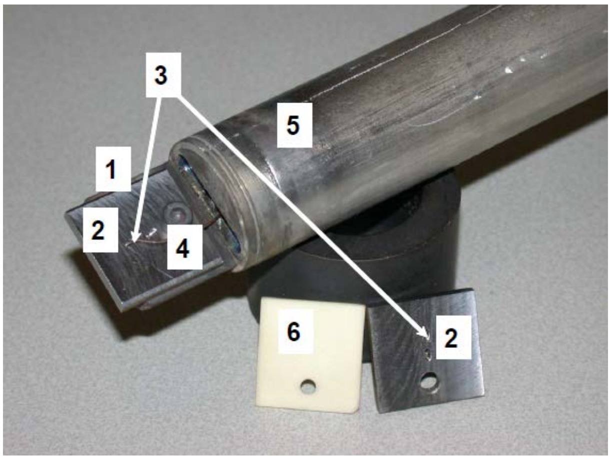


Figure 2.2 Image of the oil-cooled, vertical deposition probe for slagging/fouling investigations 1) cooling body 2) metal deposit coupon 3) thermocouple channels 4) thermocouple 5) probe body 6) ceramic deposit coupon (uncooled)

Fouling studies were carried out by means of the horizontal deposition probe, placed at a fixed distance from the burner, shown in Figure 2.3.

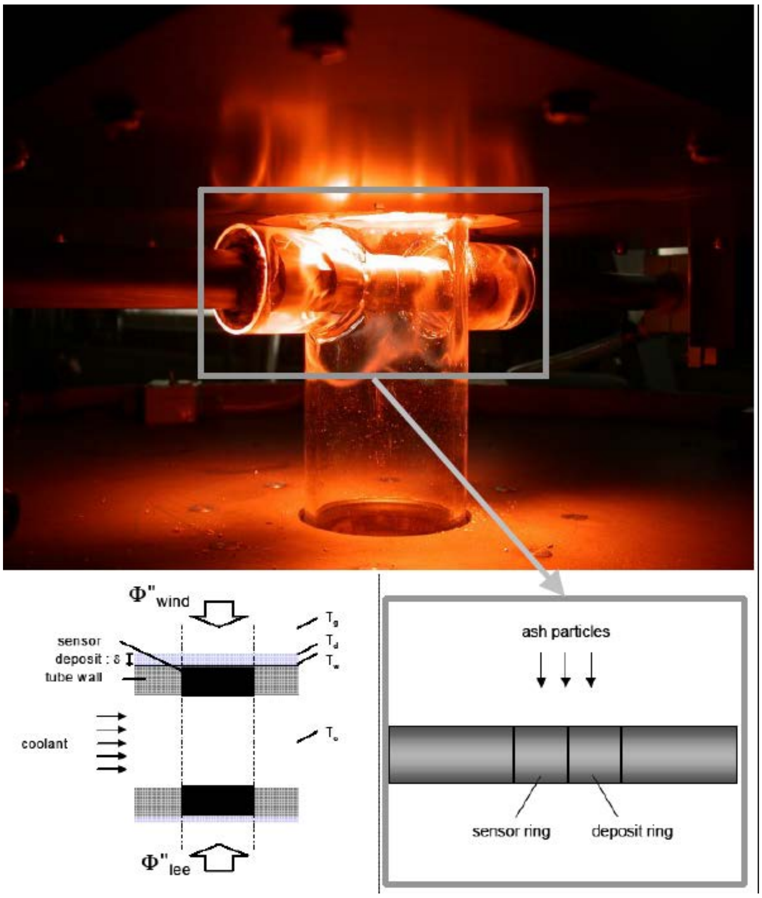


Figure 2.3 Photographs and schematics of the LCS horizontal deposition probe

The lignin Y was subjected to the slagging and fouling tests in the LCS. Figure 2.4 shows the results for the fouling tests. Fouling decreases the heat transfer to heat exchanger surfaces due to deposit build-up. Here it can be seen that very little deposits are formed. No sintering/melting is visually observed. No signs of salt condensation.

Figure 2.4 Fouling tests at the LCS with the lignin Y

The following figure shows the results obtained with the slagging tests. Slagging consists on the deposition of molten ash on the membrane walls during combustion. It can be seen that there are no molten deposits. This material seems to be safe for stand-alone firing, although there should be caution in co-firing due to the combination of Cl with alkalis present in wood.

Figure 2.5 Slagging tests at the LCS with the lignin Y

2.2.2 *Conversion & Emissions*

For these tests four lignin samples were selected: A, B, D and X (commercial lignin). Tests were carried out under conditions representing industrial pulverised fuel combustion conditions, applying burner staging (only). Gas and particle samples were taken using a suction probe that was inserted at the bottom of the reactor. A flat nucleopore filter was attached to the probe for particle separation and recovery. By determining the ash content of the partially converted char/ash particles, the burnout of the fuel under the given conditions can be determined. Furthermore, standard gas analysis was carried out during the conversion tests.

Flue gases produced by the individual lignin types were analysed for NOx emissions. By measuring the “background” NOx level generated by the gas flames and the amount of fuel fed, the specific NOx formation per unit mass of fuel fired can be calculated. The results of this calculations are given in Figure 2.6 alongside some values of other fuels for comparison. The absolute amounts of NOx formed per unit mass of fuel are specific to the air staging conditions applied in the LCS. For the values shown below, burner staging with a primary lambda of 0.85 and a total lambda of 1.15 without further (deep) staging was applied. Hence, the reported values are specific for these conditions. Even though there is a clear correlation between the fuel nitrogen content and the specific NOx formation, one can see that not only the absolute fuel-N content is determining but also the release mechanism of the fuel nitrogen, i.e. whether it is released during pyrolysis or during char burnout. When released during pyrolysis under reducing conditions, a vast part of the fuel-N can be converted to N_2, while the char-bond nitrogen is predominantly released as HCN and NO. Under oxidising conditions, the released HCN can then be further oxidised to NO.

In Figure 2.6, the specific NOx formation of the investigated lignin types is compared to the corresponding values collected for a sub-bituminous coal and two torrefied feedstocks, serving as a reference. It can be seen that all lignin samples form less NOx than the bituminous coal, even though some of them contain more fuel-N than the coal. Furthermore, the specific NOx formation of the lignin samples are in the range of typical torrefied feedstock. The lignin A performs best from the investigated fuels, indicating that NOx reduction can be expected when replacing coal with lignin, provided that at least burner staging is applied. Furthermore, probably even higher NOx reduction can be achieved when deep staging is applied.

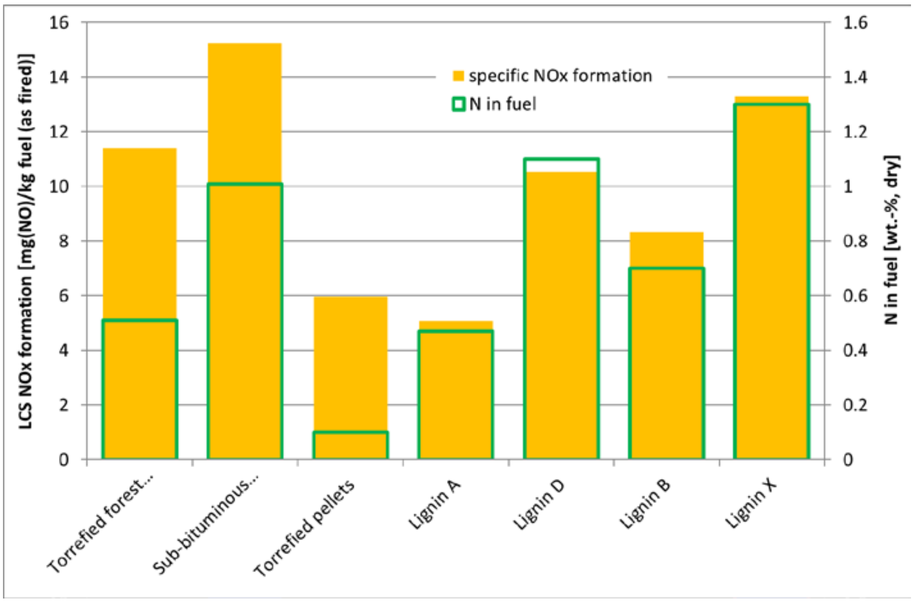


Figure 2.6 Specific NOx formation of different fuel types

Special attention should be paid to the chlorine content of lignin A because chlorine can cause severe corrosion problems. In the case that sufficient cation concentrations (for instance K or Na) are present in the flue gas, chloride salts can be formed which can cause high temperature corrosion when deposited on heat exchanger surfaces. In the case that cation concentrations are low, chlorine will leave the system predominantly as HCl vapour. The latter can also be corrosive for equipment parts, but poses less corrosion risks compared to the deposition of chloride salts, provided that the flue gas temperature is not reaching the acid dewpoint.

2.2.3 *Conclusions from LCS tests*

Both lignin Y and lignin A were tested under realistic pulverised fuel combustion conditions in the LCS. It could be demonstrated that neither significant near-burner slagging nor excessive heat exchanger fouling can be expected from the outcome of the tests. However, in a co-firing scenario with a fuel that contains cations that can react with the chlorine present in the lignin, chloride salt formation is likely to happen which can cause (alkali-) salt induced heat exchanger fouling and potentially high temperature chlorine corrosion. Nitrous oxide formation is not expected to be problematic, provided minimum burner air staging is applied. From an operational point of view, potential corrosion issues appear to form the highest risk when firing lignin A.

2.3 Gasification tests with the WOB gasifier

Lignin A was chosen for the small scale gasification tests. These experiments were carried out at the 5 kW_{th} WOB bubbling fluidized bed gasifier (electrically heated traced reactor, up to ~ 1 kg/h input fuel), schematically seen in Figure 2.7. The reactor can be electrically heated to as high as 1100°C and can be fluidized with air, steam, oxygen, nitrogen or other gases. The temperature can be controlled independently of the air supply. Bed temperatures and pressure drops are measured at four points in the bed.

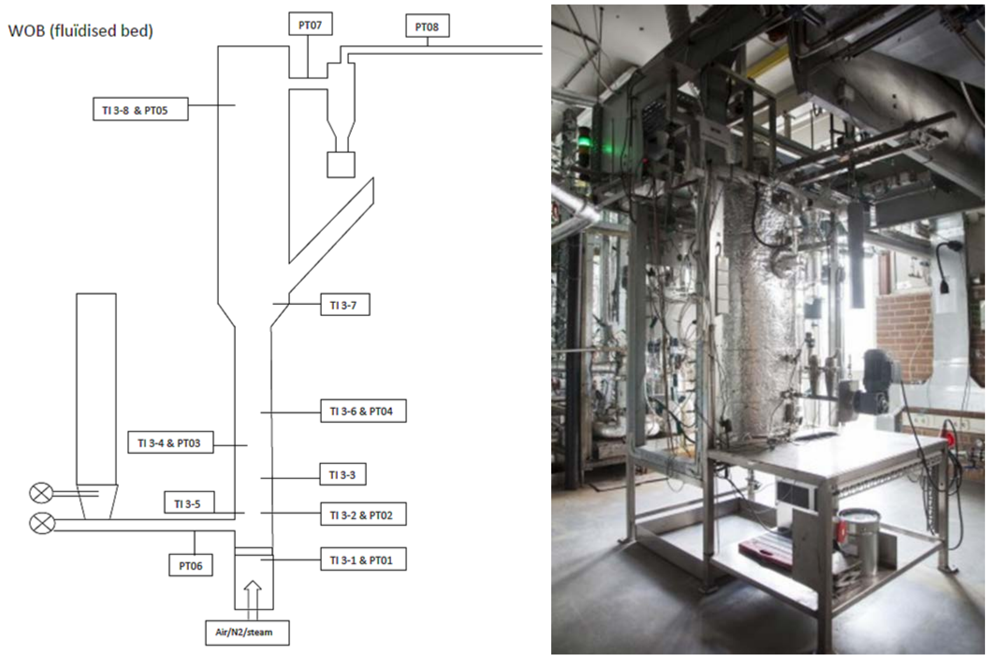


Figure 2.7 Schematic drawing of the WOB setup with pressure and temperature measuring points (left) and the WOB gasifier (right)

2.3.1 *Settings*

Two tests were performed at different temperatures: 780°C and 850°C. The reactor was pre-heated under oxidizing conditions and before the start of the tests it was flushed with N_2. For both tests the equivalence ratio (ER) [2] was kept at 0.18. Since at 780°C less gas is produced the N_2 was slightly adjusted to ensure similar fluidization conditions. About 1 kg of sand was used as bed material. Table 2.2 shows the details while Table 2.3 shows the analytical methods employed.

Table 2.2 Settings of the experimental work

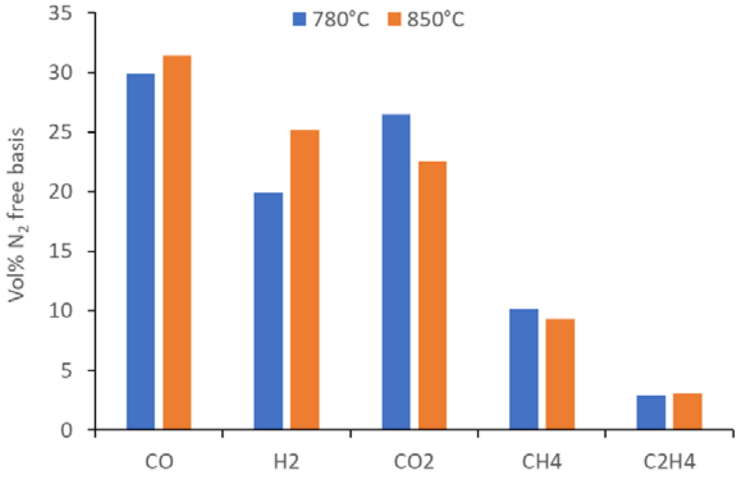
	Test 1	*Test 2*
Temperature (°C)	850	780
Bed material	Sand	Sand
Feedstock	Lignin A	Lignin A
Feedstock (g/h)	600	600
ER (-)	0.18	0.18
Air (NL/min)	10	10
N_2 (NL/min)	9	10

Table 2.3 Analytical methods employed in the experimental work

Parameter	*Analytical method*
Gas composition	• Online gas analyser (H_2, CO, CO_2, CH_4, O_2) • Online Micro-GC (CO, CO_2, CH_4, C_2H_6, C_2H_4, C_2H_2, C_6H_6, C_7H_8, H_2S, COS, N_2, Ne) • Off-line GC for hydrocarbons analysis (C_1-C_5) • Off-line GC for sulphur analysis
Tar content and composition	• Tar guideline method

2.3.2 *Results & Discussion*

The following figures show the product gas composition measured with the micro-GC on a dry N_2 free basis at the different temperatures. It should be pointed out that at 780°C the N_2 composition was about 73% while at 850°C it was about 68 vol.%.



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[2] The ratio of fuel concentration in the actual fuel-air mixture divided by the fuel concentration in a stoichiometric mixture.

Figure 2.8 Product gas composition on a dry N_2 free basis of lignin A gasification with ER of 0.18 at 780°C and 850°C

It can be seen that regardless of the temperature CO is the main component present in the product gas followed by H_2 and CO_2. The increase of temperature leads to an increase of CO and H_2 which may be the result of char gasification reactions. On the other side CO_2 seems to be reduced, while CH_4 and C_2H_4 are rather stable.

Figure 2.9 shows the results for the remaining measured gas components. It can be seen that benzene and ethane are the ones present in the largest amount, though they have opposite trends with the increase of temperature: benzene increases while ethane decreases.

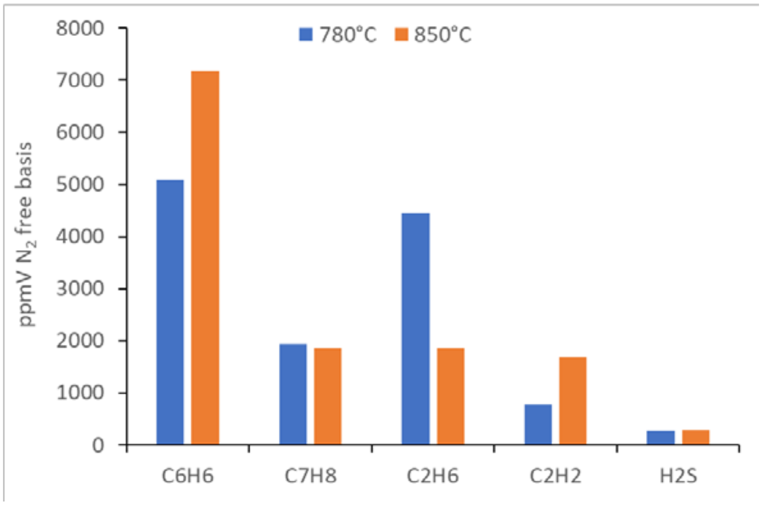

Figure 2.9 Product gas composition on a dry N_2 free basis of lignin A gasification with ER of 0.18 at 780°C and 850°C

Off-line GC analysis was performed as well for both temperatures for the hydrocarbons up to C_6 that are formed. Figure 2.10 shows the results. As can be seen there are slightly more components present at 780°C though at negligible amounts. At 850°C only acetylene (C_2H_2) and 1-3 butadiene appear with substantial values. The increase of temperature leads to a reduction of the larger hydrocarbons.

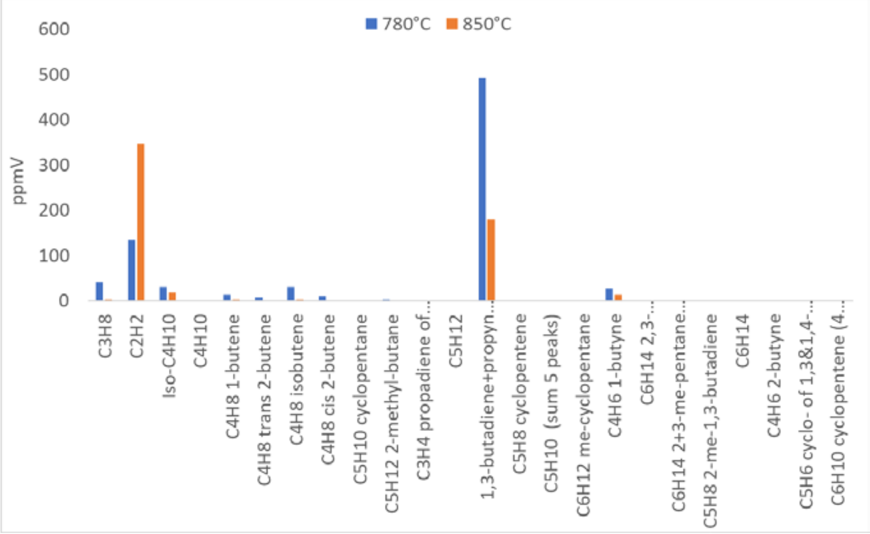

Figure 2.10 Off-line GC hydrocarbons analysis on a dry basis of lignin A gasification with ER of 0.18 at 780°C and 850°C

Tar guideline measurements were performed as well and Figure 2.11 shows the results. It can be seen that among the aromatics measured benzene is the one present with the largest amount and it increases with the increase of temperature. The same behaviour was seen with the micro-GC. Toluene does not show any substantial change, which again is in accordance with the micro-GC analysis. Naphthalene increases with the increase of temperature while phenol follows the opposite trend.

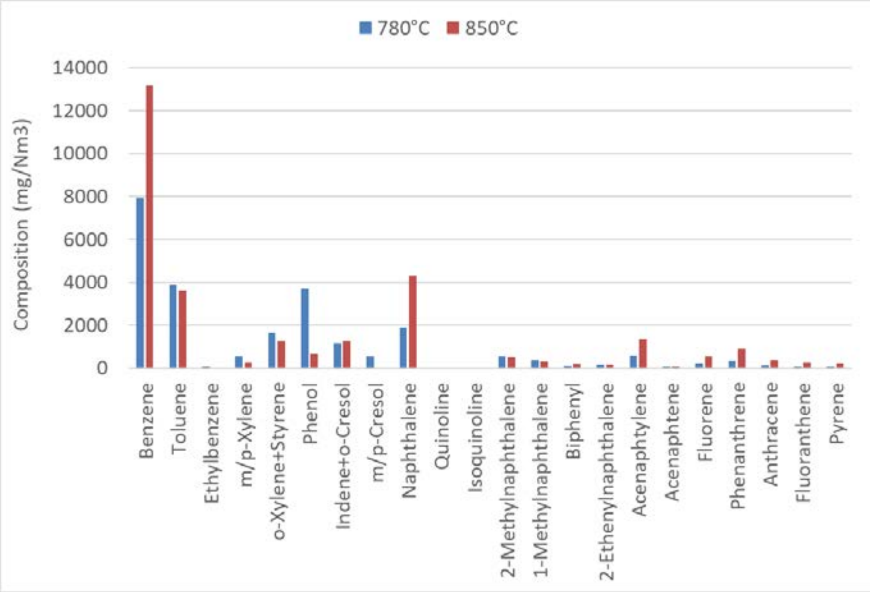

Figure 2.11 Tar guideline results of lignin A gasification with ER of 0.18 at 780°C and 850°C

Sulphur compounds were also analyzed with an off-line GC and Figure 2.12 shows the results. COS and thiophenes have the highest values. H_2S (not shown here but in Figure 2.9) was the sulphur compound present with the largest amount, with about 80 ppmV.

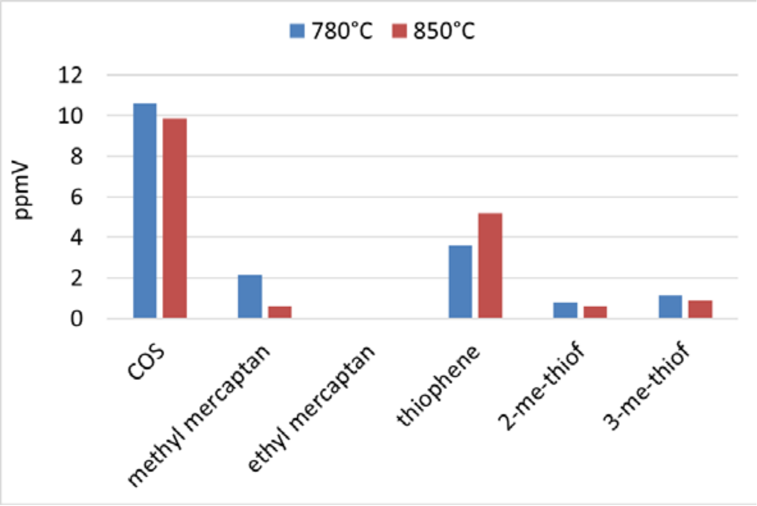

Figure 2.12 Off-line GC sulphur analysis on a dry basis of lignin A gasification with ER of 0.18 at 780°C and 850°C

In these tests Neon was used as internal standard to allow the calculation of the overall carbon mass balances. Table 2.4 shows the results where a comparison is provided with similar tests performed with beechwood and an extra test performed with beechwood in the MILENA gasifier (indirect gasification). It should be highlighted that the overall mass balances are based on terms of carbon yield which is defined as follows:

$$Carbon\ Yield\ \% = \frac{Carbon\ Product}{Total\ Carbon\ Input} \times 100$$

Table 2.4 Carbon mass balances and cold gas efficiency of different WOB gasification tests

	WOB Tests				
	Lignin A	**Lignin A**	**Beech**	**Beech**	**Milena Beech**
Temperature (°C)	850	780	850	750	850
Feedstock	lignin	lignin	beech	beech	beech
Feed (g/h)	607	607	399.8	546	-
Bed material	sand	sand	sand	sand	sand
ER	0.18	0.18	0.3	0.2	-
Product gas (C %)	56.3	49.6	93.5	80.2	78.6
Char (C %)	23.6	-	-	-	-
Tars (C %)	13.7	12.3	-	-	-
Total collected (C %)	93.5	61.8	-	-	-
Toluene (mg/g feed)	6.0	5.4	1.6	6.4	1.8
Benzene (mg/g feed)	19.7	12.0	21.4	14.4	20.2
Ethylene (mg/g feed)	30.2	24.6	27.5	31.2	37.1
Cold Gas Efficiency[3](%)	46.0	37.2	63.8	62.8	70.3

Comparing lignin with beechwood it can be seen that much less product gas is formed, which was somehow expected due to the low value of volatiles present in the lignin and seen in Table 2.1 (in the case of beechwood the volatiles account for about 81%). This is then reflected in the low value of cold gas efficiency as compared to the beechwood. To increase the value of the product gas it is necessary to increase the gasification reactions either by increasing the residence time of the solid char in the gasifier, increase the temperature or increase the amount of steam as carrier gas.

Even though the produced gas with lignin is much lower than with beech the yield of the most important components for this study (ethylene, toluene and benzene) are in the same ballpark. It is also seen that the higher the temperature the higher the formation of benzene, toluene and ethylene. It is not expected that with the increase of the gasification reactions the yield of these components will improve, though it should improve the cold gas efficiency.

2.3.3 *Conclusion*

The gasification of lignin leads to lower amounts of product gas (and as consequence larger amounts of char) though it also leads to similar values of ethylene, benzene and toluene as compared to beechwood gasification. Gasification at 850°C is preferred over 780°C since it leads to a substantial increase of benzene, toluene and

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[3] Cold gas efficiency = HHV product gas / HHV feedstock

ethylene. It is advised to use a larger amount of steam as carrier gas to improve char gasification reactions.

2.4 Conclusions

The final step in the study of the thermochemical valorization of lignin is to perform a feasibility test to validate the co-production technologies that are being developed. The conditions to be applied in the gasification process are defined based on the work developed in this chapter. Hereby lignin A is chosen for the final demonstration tests. Gasification at high temperature, 850°C, is preferred for the gas production. Also, an higher steam-biomass ratio is preferred for the improvement of the gas production of at least 0.5 kg steam/kg feedstock.

3 Adsorption of Ethylene from Producer Gas and CO_2 and Water from Reformer Gas

The Black Birds project was set up to increase the economic viability and flexibility of synthetic natural gas (SNG) production via gasification with simultaneous production of ethylene and aromatics such as benzene, toluene and xylene (BTX). Gasification of bio-refinery side streams, such as lignin from Avantium's DAWN process, will contribute to increasing the economic viability of bio-based chemicals and contribute to the development of fully integrated bio-refineries.

In Black Birds, gasification is performed in the MILENA gasifier of TNO while for tar removal OLGA technology is applied. The obtained gas contains large amounts of CO, CO_2 and H_2. Other components in the gas mixture are aromatics (~12 vol%, @35°C and 1 atm), CH_4 (~3.5 vol%), ethylene (< 2.7 vol%), water (0.4 vol%), C_2H_2 (0.4 vol%) and C_2H_6. Additionally, the mixture contains ppm levels of COS and H_2S, which can be removed by a ZnO bed. Ethylene and aromatics are valuable bulk chemicals and can be isolated before the stream is further processed to syngas (see Figure 3.1). The gas mixture needs to be cooled down to 35°C before aromatics can be stripped at ambient pressure. The next separation step is the selective adsorption of ethylene, which is the subject of this study performed by Avantium. After removal of valuable compounds the gas is further upgraded for the production of SNG.[1] The ethylene sorption unit will produce a small stream of gaseous product, which could potentially lead to logistic challenges if the plant would not be located in the vicinity of an ethylene pipeline. Therefore, TNO investigated the direct, *in-situ* aromatization of ethylene to benzene. The obtained aromatics are cycled back to the BTX scrubber and can be isolated as one liquid product.

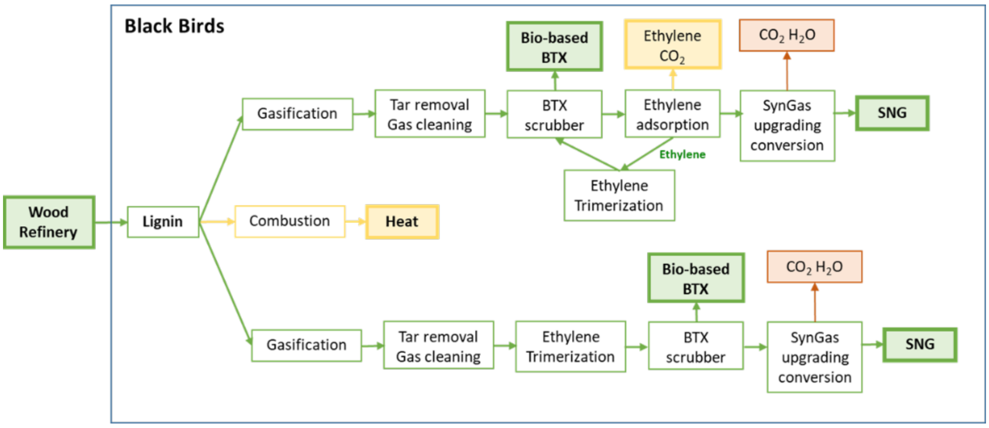

Figure 3.1 "Black Birds" schematic concept

During the Blue Bird project (TEBE115001), the sorption technology was enhanced by co-feeding water and using larger reactors to be able to use higher flows and improve flow stability. Specifically, analytics were further developed by combining mass spectrometry and GC, allowing for the discrimination of CO from ethylene and nitrogen; hence, the option for simultaneous detection of ethylene and CO_2 curves on a selected reactor.[3] In this study (Black Birds), the system was further improved:

- Evaporator was installed for improved constant water feeding to a single reactor
- Automation of the breakthrough curve

- Better insight in the composition of the adsorbed compounds at saturation point
- Prevent ethylene displacement by CO_2

Zeolites were the main material tested as adsorbents for ethylene in previous projects (Green Birds[2] and Blue Birds[3]). In literature, zeolites are reported to be good adsorbents, their capacity varying upon pore size, silica-to-alumina ratio (SAR) and ion exchangeable groups (see Table 3.1)[4-10]. In general, zeolites with a low SAR, such as zeolite A and X, have good potential as ethylene sorbent[7,10]. The effect of ion exchange on the properties of zeolites is also a well-studied subject[4-12]. It was reported that [Ag]A functions as an absolute molecular sieve and selectively adsorbs ethylene from a mixture of C_2H_6 and ethylene.[11] In the Green Birds project, [Ag]A turned out to be selective for ethylene even in the presence of water, but was not stable as sorption selectivity and capacity decreased over repeated cycles at 40°C and 5 bar_g.[13] In that same study, [Ca]A was selected as best candidate with good ethylene sorption capacities and fair selectivity with the downside of its high affinity to water.[2] During Blue Birds, zeolites A and X showed the highest potential as ethylene sorbents, however their high affinity towards CO_2 and water could not be overcome.

In Blue Birds, activated carbons showed good ethylene adsorption capacity and limited selectivity. Additionally, initial adsorption tests using metal organic frame works (MOFs) were performed. MOFs are built up from transition-metal cations, which are linked *via* coordinating multi-dentate organic groups creating an open framework that can be porous, which makes them suitable for application as a sorbent. During conventional, solvent-based synthesis of MOF small crystals are formed[13] however, in order to prevent pressure drop over the sorbent bed, the MOFs had to be pressed into larger particles which led to decrease sorption capacity.[3]

In the (current) Black Birds project, combinations of different zeolites and active carbons were made in order to tune selectivity. In order to enhance ethylene sorption selectivity, different sorbents were combined in layered or mixed beds.[3] In the first stage of the project, commercial materials are screened for their ethylene adsorption behaviour. Selected materials are subsequently functionalized (*e.g.* by ion exchange) in order to tune their ethylene selectivity, which was tested by feeding a mixture containing ethylene, CH_4 and C_2H_6. The feed complexity was increased by mixing with CO, CO_2, H_2O and H_2. Relevant properties of these molecules are listed in Table 3.2. Sorbent stability was determined over fifteen cycles of adsorption / desorption using a mock-up representing the producer gas after tar, sulphur and BTX are removed. Additional tests were addressed to CO_2 adsorption to be able to study the potential of CO_2 removal at different moments in the process (Figure 3.1).

Table 3.1 Properties of different zeolites[4,5]

Frame work	Cationic form	Window	Effective channel diameter Å	SiO_2/Al_2O_3 ratio (SAR)
A	Na	8-ring	3.8	1
	Ca		4.4	1
	K		2.9	1

X	Na	12-ring	8.4	1.3
	Ca		8.0	1.3
Y	Na		8.0	5 (and higher)
ZSM-5	Na	10-ring	6.0	30
Ferrierite	-		5.3	20

Table 3.2 Relevant properties of molecules used in the adsorption experiments[6]

Compound	Molecular weight g/mole	Kinetic diameter Å	Polarizability x 10^{-25} cm^3	Dipole moment x 10^{18} esu cm	Quadrupole moment x 10^{26} esu cm^2
N_2	28.01	3.64-3.80	17.6	-	1.52
Ar	39.95	3.542	16.4	-	-
C_2H_4	28.05	4.163	42.6	-	1.50
C_2H_6	30.07	4.443	44.7	-	0.65
CH_4	16.04	3.758	26.0	-	-
CO	28.01	3.69	19.5	0.112	2.50
CO_2	44.01	3.30-3.94	26.5	-	4.30
H_2	2.02	2.89	8.0	-	0.66
H_2O	18.02	2.641	14.5	1.87	-

3.1 Experimental Work

3.1.1 Flowrence Adsorption Unit

An Avantium Flowrence® equipment set-up was developed for adsorption experiments (Figure 3.2). The feed valve selects one reactor that is fed with the adsorption gas mixture while all other reactors are filled with nitrogen (the desorption gas). Different gas mixtures are available for testing (Table 3.3) and CO, CO_2, H_2 can be mixed with the gas feed *via* separate mass flow controllers. Gas bottles were supplied by Messer. Water is evaporated by passing the feed gas through the liquid where a water concentration of 2.3 vol% is obtained by keeping the saturator at 20°C and 0 bar_g. Afterwards, the gas is kept ≥ 35°C by using a trace line and heating of the reactors top plate. To feed dry gas, the evaporator can simply be by-passed using valves.

The system has four heated reactor blocks (40-300°C), each containing four reactors of 560 mm height, 6 mm OD and 4 mm ID. The isothermal zone was > 400 mm. During a run, one blank and 15 sorbents can be tested. Reactors are loaded with a layer of inert, non-porous Zirblast or SiC to make sure that the sorbent bed is located in the isothermal zone of the heaters.

At the reactor bottom a diluent gas (nitrogen) is mixed with the effluent for dilution prior to analysis and prevents back mixing by increasing the flow rate. The effluent oven is set at 35°C to prevent condensation after the reactors. A selector valve in the effluent is used to lead the effluent gas from the selected reactor to the mass spectrometer (Hiden Analytical) and GC (Interscience) to record breakthrough curves. A second selector valve leads the effluent from one of the desorbing reactors to the other channels of the GC to monitor desorption of CO_2, ethylene and C_2H_6.

– Gas feeds	Ethylene mix, H_2, CO, CO_2, nitrogen Can be switched on and off (= only nitrogen fed)
– Evaporator	Saturation of gas feed at 20°C Can be switched on and off

Sorbent conditioning	200°C, 25 NmL/min/reactor
Sorption temperature	40 -100°C
Sorption pressure	0-10 bar_g
Adsorption	monitored by MS and GC TCD channel (CO)
Adsorption gas flow	25 NmL/min/reactor
Desorption	monitored by two GC channels: FID (ethylene) and TCD (CO_2)
Desorption gas flow	25 NmL/min/reactor, over 16 channels (nitrogen)

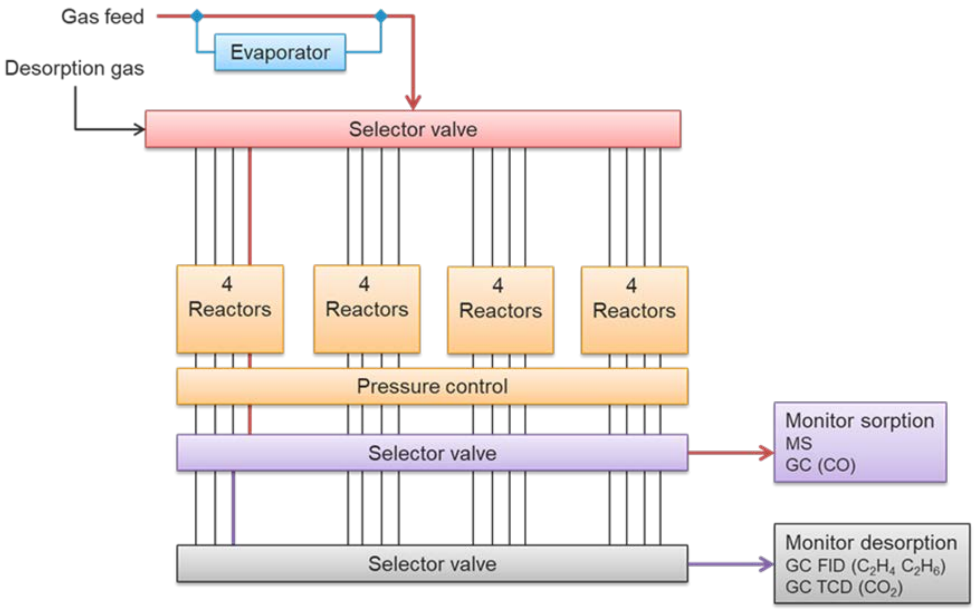

Figure 3.2 Schematic overview of the Flowrence used for the adsorption experiments

3.1.2 *Plug Flow Behaviour*

The total bed length of 350 mm includes 150 mm of Zirblast and 200 mm sorbent bed; therefore particles should be smaller than 267 μm to assure plug flow behaviour (see criteria applied below)

Bed length over particle size	$L/d_p > 50$	L= 350 mm	max d_p 7 mm
Diameter reactor over particle size	$d_r/d_p > 15$	d_r = 4mm	max d_p 267 μm

3.1.3 *Pressure Drop*

Pressure drop over de sorbent bed was calculated using the Ergun and Orning equations:

$$\Delta P/L = 150\times u\times\mu\times(1-\varepsilon)^2 / (d_p^2\times\varepsilon^3) + 1.75\times u^2\times\rho\times(1-\varepsilon) / (d_p\times\varepsilon^3)$$

ΔP	N/m^2	Pressure drop across the catalyst bed filled with spherical particles
L	m	Length of the catalyst bed
u	m/s	Linear gas velocity considering an empty tube
μ	Kg / (m × s)	Viscosity of the gas at the specified temperature and pressure
ε	-	Void fraction of the packed bed filled with spherical particles, space in between particles for the gas to flow
d_p	m	Diameter of the spherical catalyst particles
ρ	kg/m^3	Density of the gas at the specified temperature and pressure (= P×M / (R×T))

When only particles of 100 μm in at total bed length of 350 mm, a pressure drop of 0.76 bar is expected. This pressure drop decreases with increasing particle size: if the bed would be loaded with 250 μm particles a pressure drop of 0.13 bar is anticipated. The combination of plug flow and pressure drop calculations show that the particles size of Zirblast and sorbents should be 100-250 μm.

3.1.4 Gas Mixtures

Ethylene was fed from lecture bottles including 5 Vol% Argon (internal standard) and nitrogen (balance).

Table 3.3 Composition of ethylene containing gas mixtures (lecture bottles)

Mix	Vol% N_2	Vol% Ar	Vol% C_2H_4	Vol% C_2H_6	Vol% CH_4
Black1	65	5	30	0	0
Black2	65	5	10	10	10

Different gas mixtures can be obtained by mixing these with H_2, CO, CO_2 and nitrogen in different ratios. The gas concentrations to the reactor and MS are presented in Table 3.4 and Table 3.5 respectively.

Table 3.4 Feed Gas composition to the reactor.

Type	Feed section ml/min						vol% to reactor								
	H_2	CO_2	Mix	CO	Flow to reactor	Mix	H_2	CO_2	CO	H_2O	Ar	C_2H_4	CH_4	C_2H_6	N_2
C_2H_4	0	0	30	0	25	mix1	0	0	0	0	5.0	30.0	0	0	65.0
CO_2 low	0	5	30	0	25		0	14.3	0	0	4.3	25.7	0	0	55.7
CO_2 high	0	10	20	0	25		0	33.3	0	0	3.3	20.0	0	0	43.3
Producer gas 1 dry	3	3	25	3	25		8.8	8.8	8.8	0	3.7	22.1	0	0	47.8
C_2H_4 -alkanes	0	0	30	0	25	mix2	0	0	0	0	5.0	10.0	10.0	10.0	65.0
CO_2 low -alkanes	0	5	30	0	25		0	14.3	0	0	4.3	8.6	8.6	8.6	55.7
CO_2 high - alkanes	0	10	20	0	25		0	33.3	0	0	3.3	6.7	6.7	6.7	43.3
Producer gas 2 dry	3	3	25	3	25		8.8	8.8	8.8	0	3.7	7.4	7.4	7.4	47.8
Recycle test dry	5	12	20	8	25		11.1	26.7	17.8	0	2.2	4.4	4.4	4.4	28.9

Table 3.5 Composition to the MS after addition of diluent gas

Type	Feed section ml/min						vol% to reactor								
	H_2	CO_2	Mix	CO	Flow to reactor	Mix	H_2	CO_2	CO	H_2O	Ar	C_2H_4	CH_4	C_2H_6	N_2
C_2H_4	0	0	30	0	25	mix1	0	0	0	0	3.6	21.4	0	0	75.0
CO_2 low	0	5	30	0	25		0	10.2	0	0	3.1	18.4	0	0	68.4
CO_2 high	0	10	20	0	25		0	23.8	0	0	2.4	14.3	0	0	59.5
Producer gas 1 dry	3	3	25	3	25		6.3	6.3	6.3	0	2.6	15.8	0	0	62.7
C_2H_4 -alkanes	0	0	30	0	25	mix2	0	0	0	0	3.6	7.1	7.1	7.1	75.0
CO_2 low -alkanes	0	5	30	0	25		0	10.2	0	0	3.1	6.1	6.1	6.1	68.4
CO_2 high - alkanes	0	10	20	0	25		0	23.8	0	0	2.4	4.8	4.8	4.8	59.5
Producer gas 2 dry	3	3	25	3	25		6.3	6.3	6.3	0	2.6	5.3	5.3	5.3	62.7
Recycle test dry	5	12	20	8	25		7.9	19.0	12.7	0	1.6	3.2	3.2	3.2	49.2

3.1.5 Mass spectrometer:

The ions formed in the ion source of the MS are separated by a quadrupole analyser and detected by a secondary electron multiplier (SEM). The raw signal was obtained at the selected m/z values, corrected for spectral overlap and subsequently normalized to the signal of nitrogen (relative sensitivity = 1). The selected m/z values and their relative sensitivities are listed in Table 3.6. The percentage of each component is calculated based on the total normalized response.

The molecular ion peak of CO has a spectral overlaps with nitrogen at m/z = 28. The CO concentration cannot be determined using the MS, because of limited fragmentation of CO and overlap of these fragments with other compounds at m/z 12 and 16. If CO is present, it detected as N_2 signal by the MS. The N_2 signal is corrected with the CO concentration that is determined by the GC monitoring the adsorption channel.

In principle, the MS response should be linear from 0-100% concentration; however this has not been confirmed. Above 10^{-5} torr partial pressure the system is not linear but the SEM is protected against a partial pressure higher than 10^{-6} torr. Settings are selected to remain below 10^{-6} Torr for 100% N_2 and the MS is operated at approximately 1.6×10^{-7} torr.

The limit of detection (LOD) and limit of quantification (LOQ) are depending on the occurrence of other components and spectral overlap of these components. When the signal stabilized, 50 scans are used to determine the standard deviation. The LOD is defined as three times the standard deviation and the LOQ is defined as ten times the standard deviation (Table 3.6).

Table 3.6 Selected m/z values and detected compounds

Component	m/z	Spectral overlap	Relative Sensitivity	Concentration (%) average	Standard deviation	LOD / LOQ (%)
Nitrogen	28	Ethylene, C_2H_6, CO_2, CO	1	65.24	0.08	~0.2 / ~0.8
Ar	40	-	0.861	5.13	0.03	~0.1 / ~0.4
Ethylene	27	C_2H_6	0.466	9.96	0.08	~0.2 / ~0.8
C_2H_6	30	-	0.226	9.99	0.07	~0.2 / ~0.8
CH_4	15	-	1.09	10.14	0.04	~0.1 / ~0.4
CO_2	44	-	1	-	-	-
CO [a]	-	Nitrogen, Ethylene	1	-	-	-
H_2	2	CH_4, H_2O	1.18	-	-	-
H_2O	18	-	0.925	2.36	0.04	~0.1 / ~0.4
O_2 [b]	32	-		-	-	-

[a] CO is not detected by de MS due to large spectral overlap and/or a relatively low sensitivity.
[b] If O_2 is detected there is either a leakage or the sample flow is too low.

3.1.6 MS settings

– Inlet:	Hiden transient capillary 150ms
– Inlet temperature:	160°C
– Inlet flow:	1.6 NmL/min
– Detector method:	Multiple Ion Detection
– MS Source:	Cage 3.0 V Electron Energy 70.0 V Emission 50 µA
– MS Detector SEM:	Multiplier Acquisition Range 10^{-10} to 10^{-7} Torr
– Scan Time:	Approx. 5 s / scan

3.1.7 Calculation of ethylene adsorption capacity

It was assumed that Argon does not adsorb on the material. The ethylene adsorption capacity is based on the ethylene breakthrough curve. Difference in ethylene flow per time interval ($\Delta t = 10$ s) is determined as ΔEthylene = (Ethylene flow in) – (Ethylene flow out). Adsorbed ethylene per time interval is calculated as ΔEthylene × Δt. These amounts were numerically integrated to get the total absorbed ethylene (Σ_i^n $[\Delta\text{Ethylene} \times \Delta t]_i$). The ethylene adsorption capacity is reported in wt%, and should be interpreted as gram ethylene adsorbed per 100 gram sorbent.

3.1.8 Materials and bed packing

Several materials were selected for the initial screening. Commercial zeolites, carbon materials and metal oxides were obtained from Sigma Aldrich, Zeolyst, Norit, Cabot, Acros, Sasol, NorPro, Evonik, Grace Davison, PICA, Alfa Aesar, Sachtleben, Zeochem, TOSOH Corporation, Sued chemie. Fine materials were sieved to remove small particles or pressed into a pellet to obtain larger particles. Extrudes and particles > 4mm were crushed and sieved to 100-250 µm. The effect of particle size was tested for [Ca]A. Under sorbent bed a layer of inert, non-porous Zirblast (120-250 µm) or SiC (150 µm) was loaded to make sure that the sorbent bed was located in the isothermal zone of the reactor. The same diluent material was also used to fill up the space between extrudates.

3.1.9 Ion exchange of zeolites

Milli-equivalent H sites (meq_H in mmol/g) were calculated based on the zeolite SAR. The general zeolite formula is:[12]

[1] $M_{x/n}\,[(HAlO_2)_x\,(SiO_2)_y] \times zH_2O$ or

[2] $M_{x/n}\,[(Al_2O_3)_{x/2}\,(SiO_2)_y] \times zH_2O$

Assuming that no water is present and the zeolite is in the acidic form (“H-form”), the SAR equals ***y/x*** in [1] and ***2×(y/x)*** in [2]. Therefore, since $(HAlO_2)_x = (Al_2O_3)_{x/2}$, it follows that SAR = 2×(Si/Al) ratio.

[3] $\text{SAR} = SiO_2/Al_2O_3 = \text{mol}_{\text{sil}}/\text{mol}_{\text{alu}}$
$= 2 \times \text{mol}_{\text{sil}}/\text{mol}_{HAlO2}$
$= 2 \times g_{\text{sil}}/g_{HAlO2} \times (MW_{HAlO2}/MW_{\text{sil}})$

[4] $g_{\text{sil}} = (\text{SAR}/2) \times g_{HAlO2} \times (MW_{\text{sil}}\,/MW_{HAlO2})$

The mass balance for zeolite grams (g_{ZEO}) is

[5] $g_{ZEO} = g_{sil} + g_{HAlO2}$

Combining [4] and [5],

[6] $g_{HAlO2} = g_{ZEO} / [1 + (SAR/2) \times (MW_{sil} / MW_{HAlO2})]$

Therefore the number of H-sites is

[7] $\text{H-sites} = g_{HAlO2} / MW_{HAlO2} = \{ g_{ZEO} / [1 + (SAR/2) \times (MW_{sil} / MW_{HAlO2})] \} / MW_{HAlO2}$

Per g of zeolite this becomes

[8] $\text{H-sites} \sim \{ 1 / [1 + (SAR/2) \times 1.003] \} / 59.90$ (mol/g zeolite)

Metal nitrates were obtained from Sigma Aldrich, Alfa Aesar and Acros. In order to obtain maximum ion exchange 10 g zeolite [Na]A (molecular sieves 4Å, Acros) was crushed and sieved in 50-200 µm, zeolite powders were used as such. The zeolite was added to an aqueous solution of metal or ammonium nitrate. The nitrate concentration was 1 meq_H/g zeolite. The suspension was placed on the roller bank and mixed overnight at room temperature. Next, the zeolite was washed three times with H_2O. For each washing step room temperature water was added and the sample was placed on the roller bank for 15 min. The zeolites were dried for 2h at 120°C and calcined at 400°C for 2h.

3.1.10 *Functionalization MCM-41 for CO_2 adsorption*[17,18]

MCM-41 was loaded with 40 wt% organic amine. Polyethyleneimine (PEI) and tetraethylenepentamine (TEPA) were introduced by wet impregnation with and without alkaline treatment of MCM-41. The organic base was dissolved in 10 mL ethanol and 1 g MCM-41 was added. The obtained slurry was placed on a roller bank (40 rpm) at room temperature for 1h and subsequently left for overnight to settle. The precipitate material was dried for 8h at 80°C. After impregnation the MCM-41 powder was pressed into pellets and shaped into 150-250 µm particles. For the alkaline treatment method, the organic base was dissolved water with 1 wt% $Ca(OH)_2$ and the obtained precipitate was dried at 100°C.

3.2 Results & Discussion

3.2.1 *Analysis of breakthrough curves and sorption capacity of [Ca]A*

3.2.1.1 *Adsorption curves*

Our previous research showed that [Ca]A is a good and stable sorbent for ethylene and is well-studied in literature.[2,3] It was therefore selected as the reference material for our tests and used to determine the reproducibility of the sorption tests.

Adsorption of ethylene from more complex gas mixtures is monitored for 45 min by the MS and GC, a typical adsorption experiment of ethylene on [Ca]A is plotted in Figure 3.3. Nitrogen and Argon are always present in the gas mixture as balance gas and internal standard, respectively. In the first data points, ethylene and Argon from the lines between the selector valve and the MS are observed as cross-over. Next, 100% nitrogen is observed while the reactor fills up with the mixed feed gas. The breakthrough of the internal standard is considered as the start of the measurement.

In this example, breakthrough of ethylene is observed after ~13 min, but this varies strongly depending on sorbent properties, temperature and pressure. The longer it takes until breakthrough is observed, the more ethylene is absorbed. Ethylene sorption capacity is determined for different sorbents at different conditions. An example of adsorption from a more complex gas mixture is given in Figure 3.4, the breakthrough curves of CO, CO_2 and ethylene can be observed in this plot where H_2 is not absorbed. The shape of the breakthrough curves can give information about plug flow behaviour in the reactor and kinetic limitations. Plug flow behaviour is best monitored in the breakthrough curve of Argon. All reactors were filled up with a diluent (SiC and/or Zirblast) to improve plug flow behaviour. Zirblast gave the best results in improving plug flow behaviour. SiC showed less retention of water and was therefore used for the later runs. Adsorption is a fast phenomenon and upon saturation breakthrough occurs within seconds and results in a sharp curve from 0 to 100% concentration of the absorbed species. When breakthrough is slow, the adsorption can be kinetically limited by, for example, the sorbent pore size. For example, the pore size of [Na]A of 4 Å is close to the kinetic diameter of ethylene, leading to diffusion limitations. This effect was studied for different types of zeolite A during the Green Birds project.[2,13]

The influence of sorption conditions on the ethylene sorption capacity is illustrated in Figure 3.5. Co-adsorption of CO_2 leads to a decrease in capacity for ethylene. A trend of decreasing sorption capacity with increasing temperature is observed and can be explained based on the fact that adsorption is an exothermic process. This trend also confirms the absence of kinetic or diffusion limitations. It was observed that the adsorption capacity increases with pressure as more molecules can fit in the pores at higher pressures. The ethylene adsorption capacity of [Ca]A determined in 42 experiments at 40°C and 0 bar_g (red circle highlighted data points in Figure 3.5) and resulted in an average of 5.0 ± 0.5 wt% (Table 3.7).

Table 3.7 Statistics on ethylene adsorption of [Ca]A at 40°C and 0 bar_g based on 42 experiments

Measure	wt%
min	4.1
max	5.9
average	5.0
standard dev.	0.5

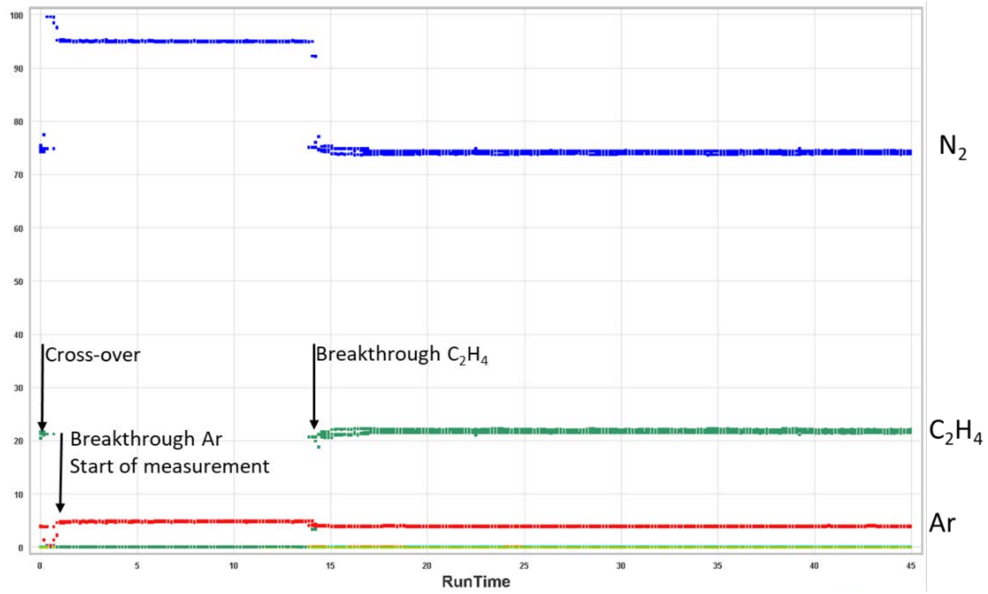

Figure 3.3 Typical breakthrough curve of ethylene on [Ca]A. indicated are the cross-over from the previous reactor, start of the measurement and breakthrough of ethylene.

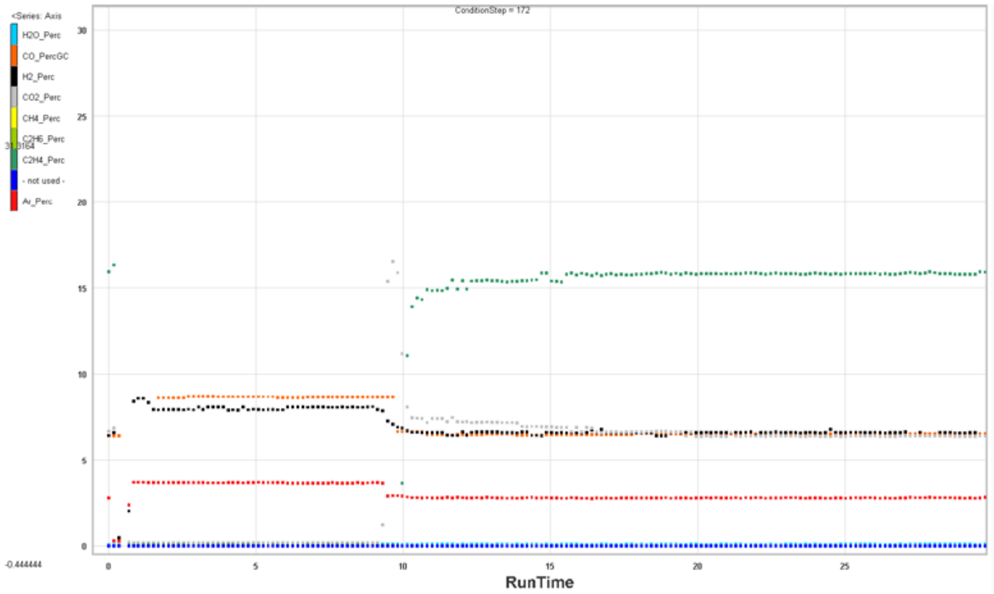

Figure 3.4. Adsorption from a gas mixture containing ethylene, CO_2, H_2 and CO. Nitrogen not plotted for clarity

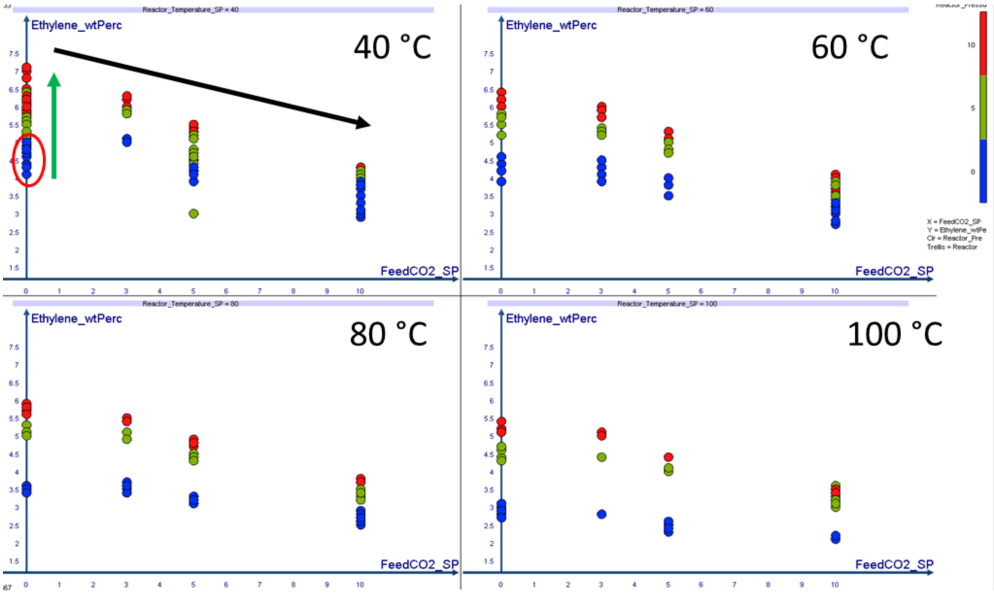

Figure 3.5. Ethylene sorption capacity of [Ca]A under different temperatures, reactor pressures and increasing amounts of CO_2 mixed in. Black arrow indicates increasing CO_2 in stream, green arrow indicates increasing reactor pressure

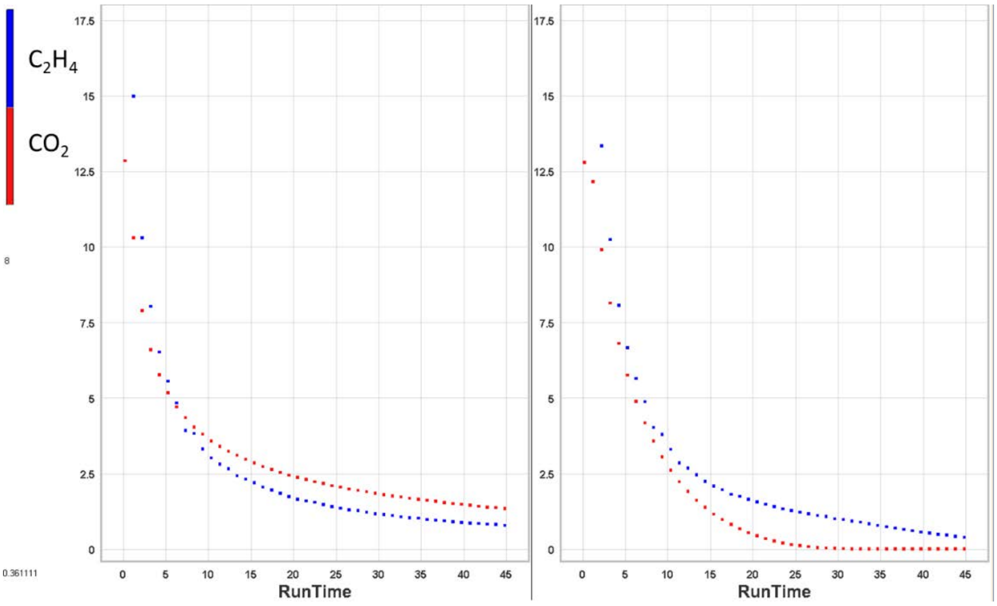

Figure 3.6. Desorption curves of ethylene (blue) and CO_2 (red) from [Ca]A at 0 bar_g at 40°C (left) and 100°C (right). The feed during the preceding adsorption step contained 5 ml/min CO_2

3.2.1.2 *Desorption curves*

Typically, strong adsorbent will release the sorbate slowly during the desorption step. Desorption of ethylene and CO_2 is monitored for 45 min by GC and can be used to get qualitative information about the composition of the desorbed gasses. An example of the resulting curves is depicted in Figure 3.6. CO_2 desorption is much slower compared at 40°C than at 100°C, where pure ethylene was observed after 25 min. This shows that pure ethylene (in the desorption gas N_2) can be collected from an ethylene-CO_2 mixture.

3.2.2 Ethylene adsorption on different materials

3.2.2.1 Zeolites

The ethylene adsorption capacities for different zeolites were determined (Figure 3.7) where low SAR zeolites (A and X) showed the highest sorption capacity at 40°C and 0 bar_g. In general, sorption capacity increased with increasing pressure and decreased when the temperature was increased to 100°C, which is consistent with an exothermic adsorption process. Remarkably, ZSM-5 and [Na]A showed a decrease in sorption capacity when the test was repeated. This could be attributed to a loss of porosity by breakdown of the material or to incomplete desorption of ethylene

The highest ethylene adsorption capacity was observed for 13X and [Ca]A. The lower adsorption on [Na]A and lack of adsorption of ethylene on [K]A can be related to the smaller pore sized of these materials. The adsorption capacity of zeolite X was less affected by ion-exchange of the material as the pore size of this zeolite is much larger than the kinetic diameter of ethylene (Table 3.2). Zeolites are known to have a very high affinity towards water. Therefore, drying of the gas mixture or addition of an additional sorbent layer for the removal of water will be required when zeolites are used as adsorbent. Ion-exchange of [Na]A with Mg^{2+} or Mn^{2+} did not significantly improve the capacity or selectivity towards ethylene compared to [Ca]A. Ion-exchange with Ag^+ resulted in a very selective sorbent for ethylene from C_2H_6 and CO_2, but with lower stability as shown before in the Green Birds project.[2,13]

3.2.2.2 Carbon

Selection of carbon based sorbents was based on the Blue Birds project results and the carbons with the highest affinity for ethylene were chosen.[3] Most of these materials had a similar ethylene sorption capacity, but GCN3070 showed the best performance with 5 wt% ethylene adsorption at 40°C and 0 bar_g (Figure 3.8). Increased reactor temperature led to a decrease in sorption capacity, while increase pressure improved sorption capacity to 11 wt% (5 barg) and even 14 wt% (10 bar_g). Co-adsorption of CO_2 was observed, but the ethylene capacity hardly decreased in this case. When C_2H_6 was present, a higher affinity to C_2H_6 was found, leading to a decreased sorption of ethylene.

The desorption curves in Figure 3.9 indicate that pure ethylene can be desorbed from carbon. When comparing the desorption curves of ethylene and CO_2 from zeolite and carbon, the low adsorption CO_2 on carbon is very clear while , at the same conditions, a mixture of CO_2 and ethylene is obtained from zeolite [Ca]A.

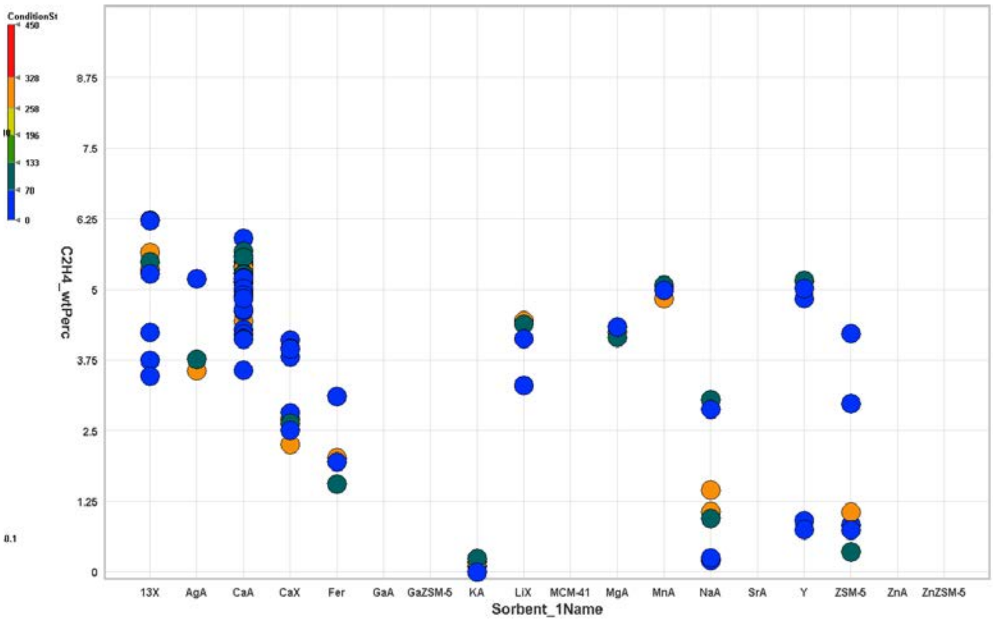

Figure 3.7 Ethylene sorption capacities determined for different zeolites at 40°C and 0 bar_g. Color scale blue-red indicate increasing number of adsorption-desorption cycles

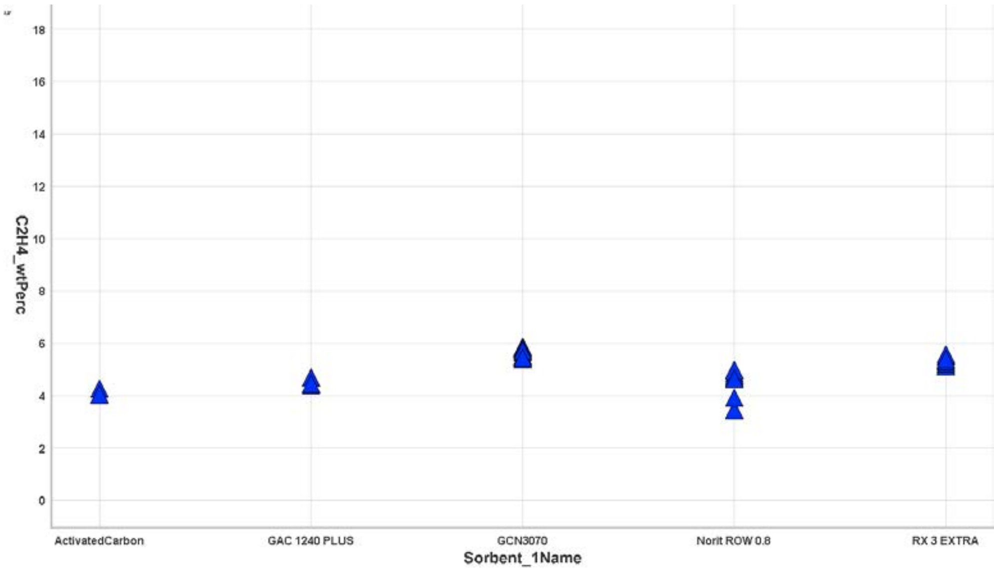

Figure 3.8 Adsorption of ethylene on different carbon based adsorbents at 40°C and 0 bar_g

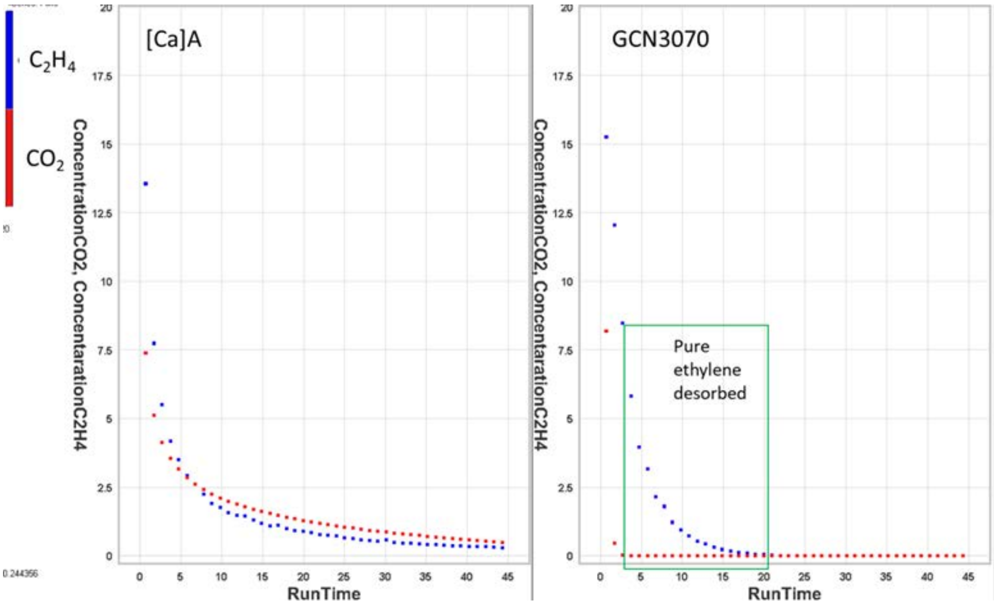

Figure 3.9 Desorption curves of ethylene (blue) and CO_2 (red) from [Ca]A (left) and carbon GCN3070 (right). The time frame where pure ethylene can be desorbed is indicated by the green frame. 40°C, 0 bar_g, 5 ml/min CO_2 in main feed

3.2.2.3 Combined beds

Different sorbents have shown different selectivity's and these could be combined by layering different sorbents for an overall optimal bed. For example, if [K]A, [Na]A and [Ca]A are layered from top to bottom: water is ideally removed by [K]A, CO_2 taken up by [Na]A and ethylene is selectivity adsorbed by the [Ca]A layer. In our tests, this combination of zeolites only resulted in a decreased ethylene adsorption capacity and no benefit was observed. This could be improved once desorption pressure and temperature can be controlled independently from the adsorption settings.

Combinations of carbon and zeolite beds did not result in increased ethylene adsorption selectivity or capacity; in contrast, the sorbents order impacts desorption gas composition (Figure 3.10). When the gas is first led through a carbon bed and then over [Ca]A, ethylene can be selectively desorbed. The ratio of different materials was also a key factor, as larger proportions of zeolite showed to delay desorption and decrease selectivity (Figure 3.11). This effect was especially clear at 100°C and 0 bar_g. It is interesting to note that a total physical mix of carbon and [Ca]A (i.e. opposite to layering) showed no separation between ethylene and CO_2. Advanced desorption with programmed temperature and/or pressure swing could help to selectively desorb one compound.

3.2.2.4 MCM-41

MCM-41 can adsorb up to 10 wt% CO_2 at high pressures and feed flow (Figure 3.12 and Figure 3.13). MCM-41 was modified with organic amines PEI and TEPA in order to improve the CO_2 adsorption properties.[17,18] When the material was modified with TEPA, an increased CO_2 adsorption and decreased ethylene adsorption compared to the parent material was observed at 0 bar_g. This positive effect was reduced when increasing pressure to 5 and 10 bar_g. Materials impregnated with PEI showed less CO_2 adsorption capacity compared to the original MCM-41, which was not affected by addition of $Ca(OH)_2$ during the impregnation.

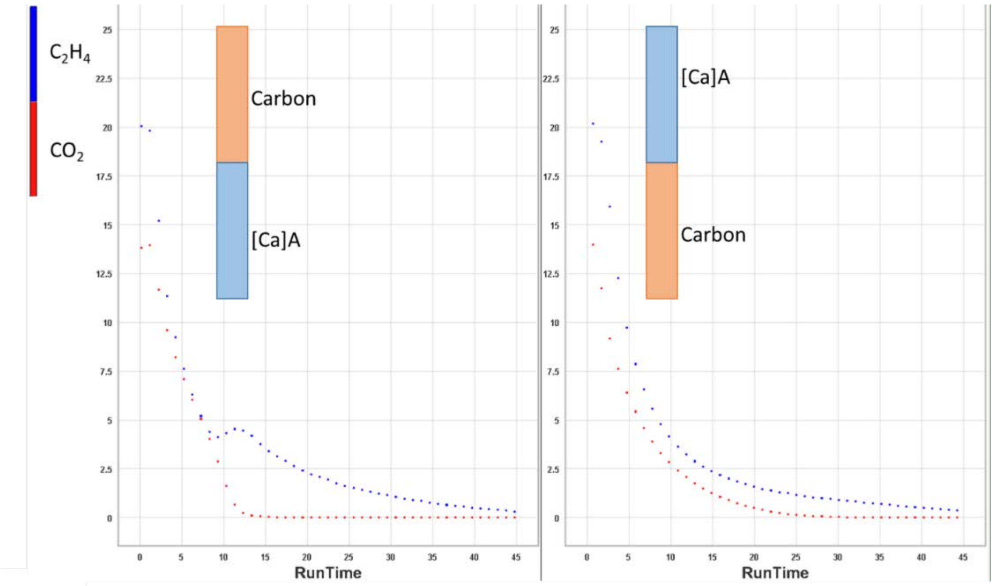

Figure 3.10 Desorption of ethylene (blue) and CO_2 (red) from layered beds based on carbon (GCN3070) and zeolite [Ca]A. Desorption at 100°C and 0 bar_g. Feed during adsorption contained 5 ml/min CO_2. Order of the different layers influences the composition of the desorbed gas mixture.

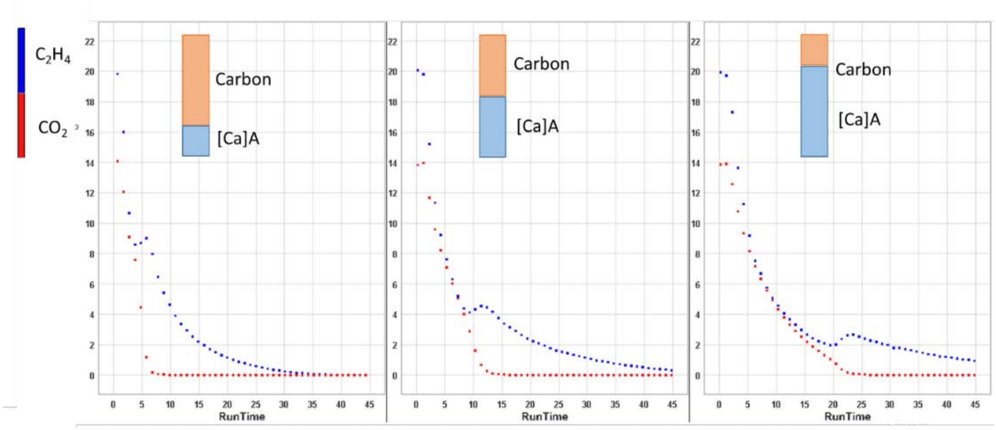

Figure 3.11 Desorption of ethylene (blue) and CO_2 (red) from layered beds based on carbon (GCN3070) and zeolite [Ca]A. Desorption at 100°C and 0 bar_g. Feed during adsorption contained 5 ml/min CO_2. Left to right increasing portion of [Ca]A bottom layer.

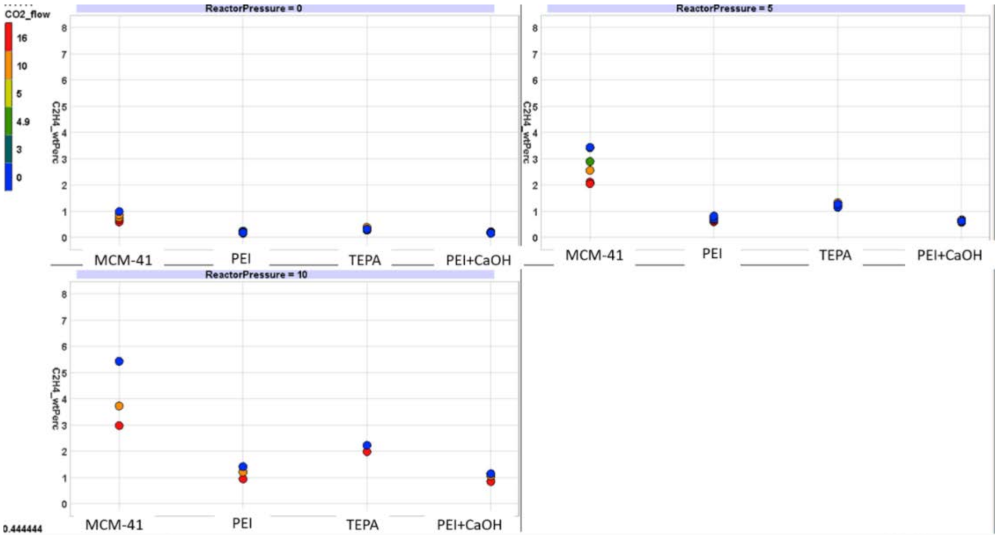

Figure 3.12 Adsorption of ethylene on MCM-41 and MCM-41 modified with organic amines. At different reactor pressures and CO_2 feed flows at 40°C.

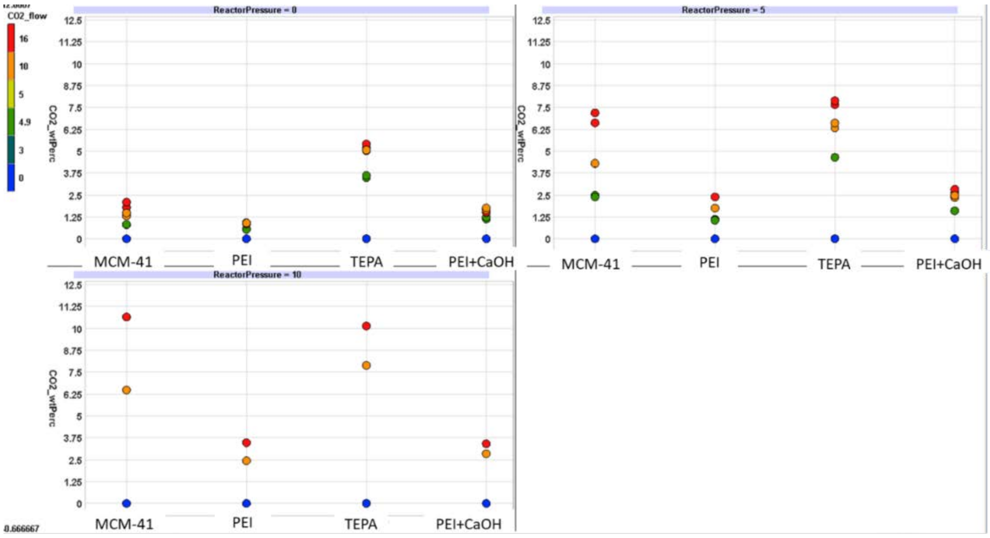

Figure 3.13 Adsorption of CO_2 on MCM-41 and MCM-41 modified with organic amines. At different reactor pressures and CO_2 feed flows at 40°C.

3.2.3 *Recommendations for kg scale adsorbent test at TNO*

Based on the materials sorption capacity and selectivity, a selection was made for a stability test using mock up producer gas at 40°C and 5 bar_g. The dry gas mixture contains 11.1 vol% H_2, 26.7 vol% CO_2, 17.8 vol% CO, 4.4 vol% C_2H_4, 4.4 vol% CH_4, 4.4 vol % C_2H_6, 28.9 vol% N_2 and 2.2 vol% Ar. First 15 cycles were performed using a dry gas stream. These were followed by 5 cycles with water-saturated gas and one cycle with dry gas to check for sorbent degradation by water. Calculated sorption capacities for single layer and multiple layer sorbent beds are reported in Figure 3.14 and Figure 3.15 , respectively.

Zeolites and carbon showed stable operation. Little effect of water was observed in the zeolites and could be related to the low concentration of water, which is not sufficient to fully saturate the material hence making ethylene adsorption still possible. Carbon and zeolites (molecular sieves) are good candidates due to their good sorption capacity, high stability and commercial availability. It was shown that carbon has a low affinity towards CO_2. In addition, pure ethylene can be obtained from ethylenye-CO_2 mixtures, when carbon or carbon-zeolite combinations are used. Co-adsorption of alkanes was observed for both zeolites and carbons but stronger for the latter.

Shaped materials are known to have limited strength and should be carefully selected to avoid pressure drop over the sorbent bed and maintain plug flow behaviour. A binder is often used to produce extrudates with appropriate strength, but this can strongly influence the sorption capacity and selectivity of a sorbent (Green birds[2]).

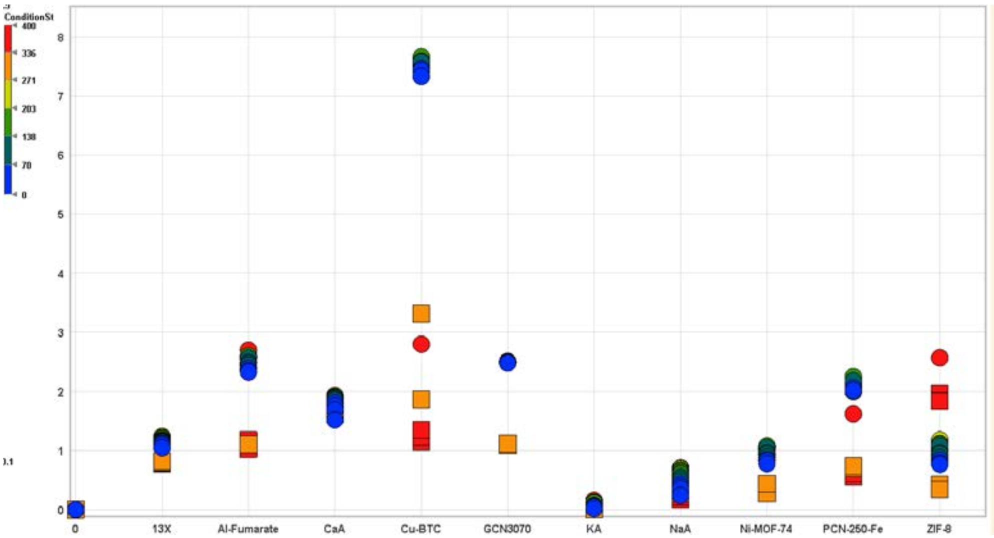

Figure 3.14 Stability of selected sorbents under mock up producer gas at 40°C and 0 bar_g over 15 cycles without water (circles), followed by 5 cycles with water vapor (squares) and 1 cycle without water. Colours (blue to red) indicate increasing adsorption-desorption cycle number.

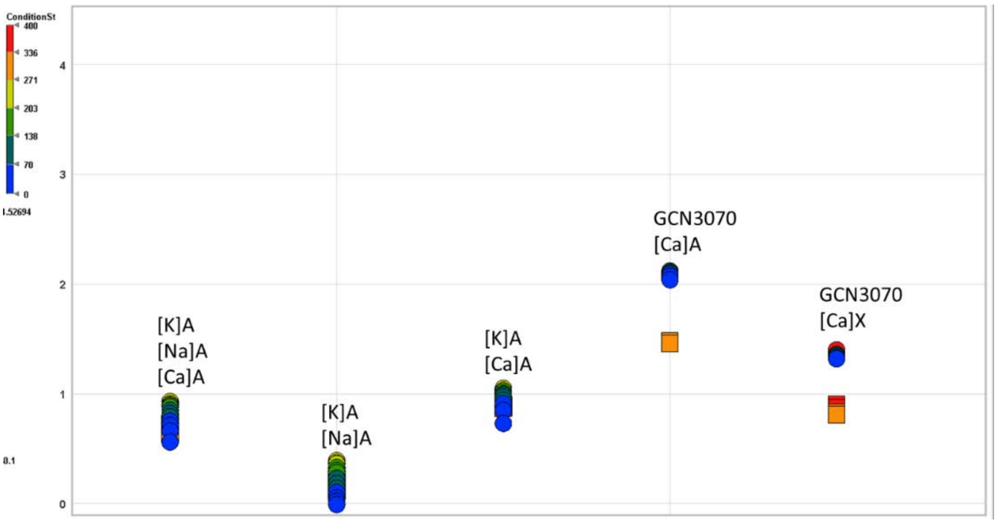

Figure 3.15 Stability of selected layered sorbent beds under mock up producer gas at 40°C and 0 bar_g over 15 cycles without water (circles), followed by 5 cycles with water vapor (squares) and 1 cycle without water. Colors (blue to red) indicate increasing adsorption-desorption cycle number.

An adsorption column containing 500 g will be installed at TNO and fed with producer gas from lignin gasification. Some gas purification is required before ethylene adsorption: tar will be removed using OLGA and a ZnO bed will be installed to remove sulphur compound. It is also recommended to install the ethylene adsorber after the AREA as BTX can adsorb on the sorbent surface and block the materials pores. Dilution of the sorbent bed with a non-porous material is required to dissipate the heat generated during exothermic adsorption. In the previous Blue Birds project, Al_2O_3 was used for this purpose. At 40°C 0 bar_g, ethylene was not absorbed on ZnO and Al_2O_3, however at 5 bar_g a sorption capacity of 1 wt% ethylene was found. For this reason and the potential reactivity of Al_2O_3, the use of Zirblast or SiC is preferred over Al_2O_3 as diluent material.

3.2.4 Automation of the adsorption curve detection

Adsorption experiments are relatively fast events and require for fast analytics to avoid conflicts in the cycle time of (online) analytics, *i.e.* the method not being able to keep up with occurring events. This is a relatively rare event in single reactor or sequential experiments because the simplicity of the system allows for continuous monitoring of one reactor. In parallel reactor systems, however, the time interval between measurement points is directly determined by the number of reactors to be measured by a single analytical device. Adding multiple analytical devices is impractical in terms of cost and data consistency, hence reverting to a sequential reactor set up is often the regretted solution of choice. Automation is a key development here where efficiency gains cannot be found elsewhere.

In adsorption experiments, a gas mixture is passed over a material where one (or more) species will be adsorbed. Once the bed is saturated and cannot adsorb anymore, the outlet gas composition will be identical to the inlet feed; this is commonly known as breakthrough. The capacity of the adsorbent can be derived from the time to breakthrough and the amount of adsorbed species. Up front determination of the cycle time needed to capture all breakthrough events for a mixture is difficult; hence, this means that one would select a rather conservative time for an adsorption cycle in practice. As parallelization of the sorption equipment is challenged by the analytical settings required to record the breakthrough curve, one can reduce experimental time by automation.

Figure 3.16 shows typical transient breakthrough experiments for multi-component adsorption executed in the Black Birds project. At the selected reactor loadings and flow settings, breakthrough events can take place anywhere between 1 and 40 min, so a fixed cycle time of 45 minutes would be a logical choice when considering a single reactor. With 16 reactors, typically evaluated over hundreds cycles, automated detection would help save time and cost to experiment duration.

Several methods were evaluated using the generated experimental data from Black Birds and Blue Birds to increase the available dataset:

1. Curve fitting methods yield a very accurate description of the data and breakthrough depiction, provided that an appropriate model is selected; however, they require a relatively large amount of data and are sensitive to experimental noise (especially outliers). Therefore, these are not the most suitable methods for real time detection.

2 Thresholding methods provide a more robust alternative here. This method is based on the selection of an appropriate base line level and breakthrough is detected when the measured signal rises from *ca.* null to a certain fraction of the baseline. It follows that the level baseline fraction provides a means to control the sensitivity of detection. A representative example is provided in Figure 3.17. In an ideal case, the baseline level for a species coincides to the inlet feed concentration of the species but deviations might occur. As a best practice, Avantium uses the first cycle in a series of measurements to determine the appropriate baseline level. This value can be used throughout a multi-cycle experiment or re-determined periodically by measuring a full cycle at appropriate times. Note that the initial measurements are ignored because they do not represent an adsorbent bed fully contacted with the gas mixture.

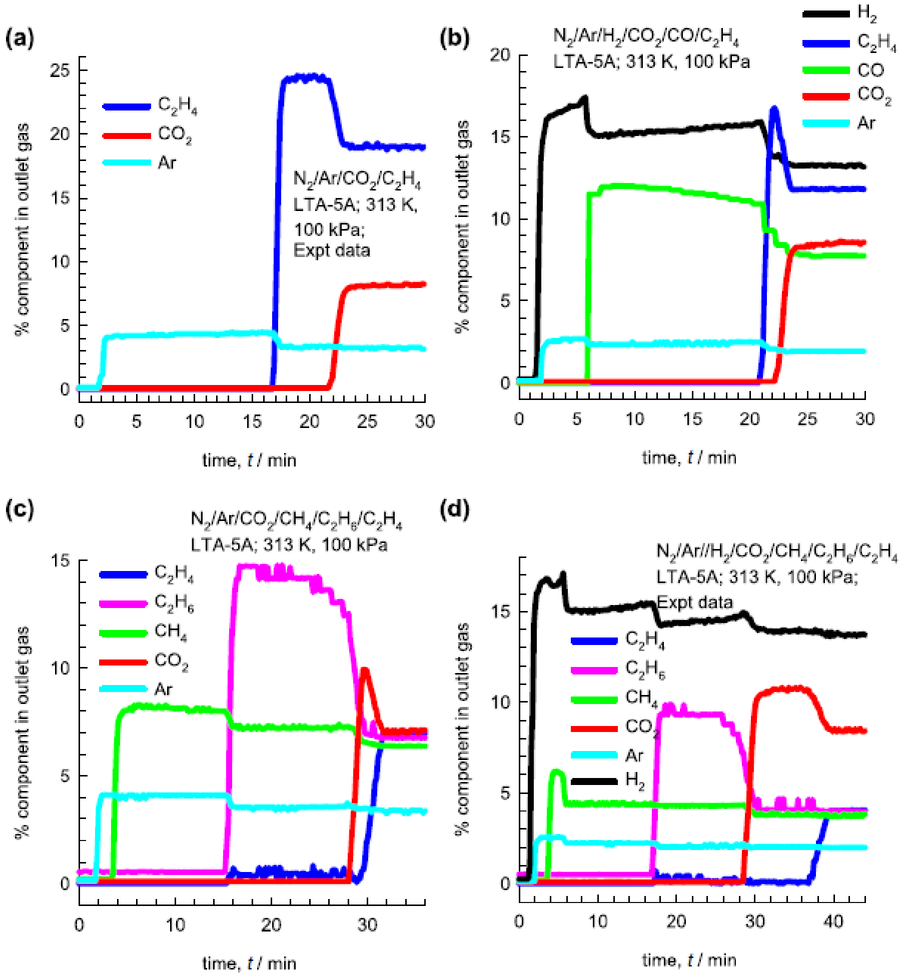

Figure 3.16 Transient breakthrough experiments for different gas compositions encountered in an application. Mind the different time scale for each subplot a through d (taken from Separation and Purification Technology 227 (2019) 115730).

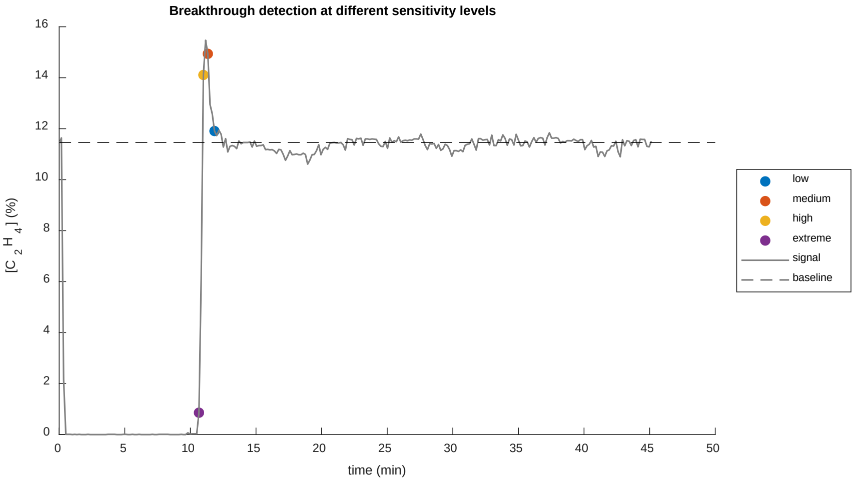

Figure 3.17 Detecting ethylene breakthrough over a selected adsorbent at different sensitivity levels

Avantium selected a thresholding method for the evaluation of the adsorption data in the 16-parallel unit; explained here for an experiment with two different adsorbents exposed to a mixture of ethylene and carbon dioxide in nitrogen. After adsorption is completed, the feed is switched to nitrogen for desorption, while the next reactor undergoes its own adsorption cycle. It follows that since desorption is typically much faster, the limiting step determining the experiment duration is the adsorption cycle (number and duration). A fixed duration of 45 min and a total of 15 cycles results in 22.5h experiment time.

Automation of detection can provide a clear gain here, as illustrated in Figure 3.18 . Material A shows a constant adsorption/desorption breakthrough pattern. In contrast, material B shows a clear non-stationary state behaviour where breakthrough times for ethylene vary widely. The breakthrough curve for a wide range of carbon dioxide concentrations remains virtually constant. Implementing a thresholding detection strategy results in a maximum experimental time of 6.7h, *i.e.* only 30% of the pre-programmed cycle time is required. The gain is visually shown in Figure 3.19 and is especially relevant for the industrially applied scenarios where 100-500 cycles are required, making the time and cost gain tangible.

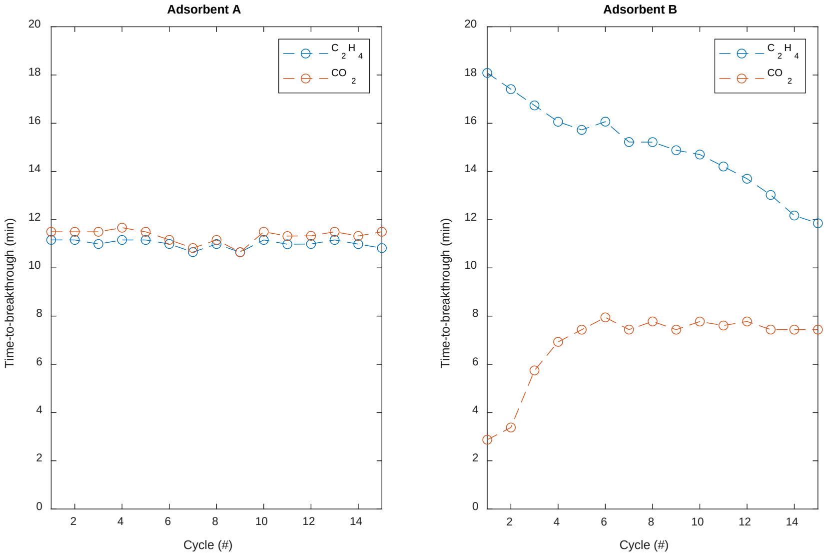

Figure 3.18 Time-to-breakthrough for ethylene and carbon dioxide for two different adsorbents measured over 15 consecutive adsorption cycles. Between each adsorption cycle, desorption was accomplished by passing a flow of nitrogen over the adsorbent beds

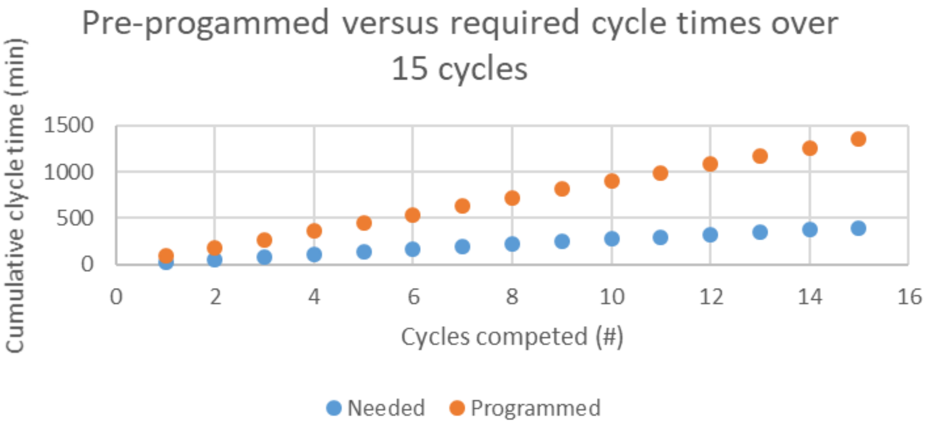

Figure 3.19 Time gain obtained by automated breakthrough detection over 15 completed cycles

To make an efficient use of the developed methodology, implementation at the equipment control software level is required: data will be evaluated while being generated and stored in the data warehouse. If criteria for breakthrough are met, the control software can switch the evaluated reactor to “desorption” and the next reactor in sequence to “adsorption”. A schematic of the implemented logic per reactor is provided in Figure 3.20 . All required calculations are implemented in an SQL script and the underlying database on a Microsoft SQL server platform. If alternative data storage technologies are to be used, the calculations required are sufficiently simple to provide options for a quick methodology migration. The control software provides the user with access to parameters to control detection sensitivity, the number of cycles per reactor and the frequency of full cycle runs to determine baseline levels.

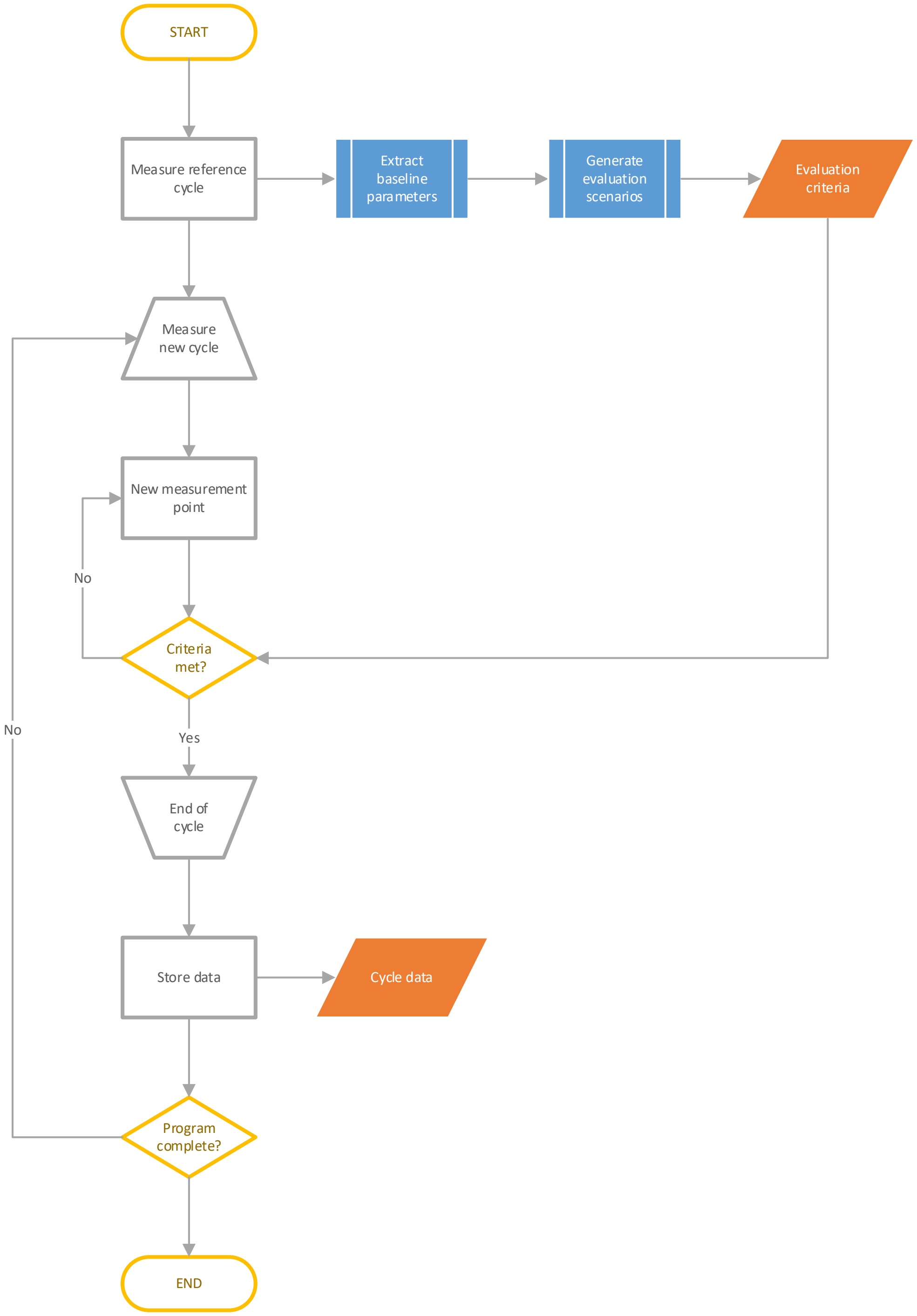

Figure 3.20 Control logic applied to a single reactor for breakthrough detection in an automated manner

3.2.5 *Modelling in collaboration with University of Amsterdam (UvA)*

UvA's Professor R. Kirshna modelled part of the sorption data recorded for [Ca]A using Ideal Adsorbed Solution Theory (IAST) and Real Adsorbed Solution Theory (RAST). It was shown that the non-ideal behaviour of CO_2 leads to an under-estimation of the ethylene selectivity. It was found that at C_2H_4/CO_2 ratios > 1, a high selectivity for ethylene is found. These findings resulted in two publications out of this work and can be found in:

- Ilona van Zandvoort, Jan Kees van der Waal, Erik-Jan Ras, Robbert de Graaf and Rajamani Krishna *“Highlighting non-idealities in C2H4/CO2 mixture adsorption in 5A zeolite”, Separation and Purification Technology* **2019***,* 227, 15, 115730
- Ilona van Zandvoort, Erik-Jan Ras, Robbert de Graaf and Rajamani Krishna *“Using Transient Breakthrough Experiments for Screening of Adsorbents for Separation of* C_2H_4/CO_2 *Mixtures” Separation and Purification Technology* 2020, Vol 241, 116706

3.3 Conclusions

The following is concluded:

- None of the tested material can separate alkanes from ethylene.
- Selected activated carbons showed the best selectivity towards ethylene from $CO_{2.}$
- Zeolite [Ca]A and carbon GCN-3017 or combinations of these materials are the best options for ethylene adsorption from producer gas.
- For selective CO_2 removal [Na]A or MCM-41 are suitable adsorbents. Specifically, TEPA-treated could be used for better capacity and selectivity at lower pressure.

3.4 References

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4 Catalytic Aromatization of ethylene

In the previous Birds projects Ga-ZSM5 was identified as a suitable catalyst capable to convert about 99% of ethylene with a 60% selectivity into BTX[4]. A duration test of about 30 hours showed a slight deactivation, however, after regeneration with air the catalyst recovered its initial activity. In a review performed by Catalok, Zn was identified as another interesting metal that could be an option for converting ethylene into aromatics. To obtain more insight into the mechanism of this reaction a parametric study was commissioned to the University of Ghent. Two different types of catalyst were prepared and tested using two different gas mixtures. Variables tested were GHSV (Gas Hourly Space Velocity), temperature and pressure. In this section a summary of the results will be given.

Additionally, a review on the potential role of Zn as a substitute for Ga in ethylene aromatization was performed by Catalok. These new findings in conjugation with the previous work developed in Blue Birds have resulted in a peer review paper:

- C.M. Lok, J. Van Doorn, G. Aranda Almansa; "*Promoted ZSM-5 catalysts for the production of bio-aromatics, a review*"; Renewable and Sustainable Energy Reviews 113 (2019) 109248.

4.1 The Potential of Zinc as an Alternative to Gallium in the Conversion of Ethylene and Lower Alkanes into Aromatics

Earlier the literature on the aromatization of ethylene was reviewed with an emphasis on Ga-promoted ZSM-5 zeolites as catalysts (Lok, 2017). Subsequently Zn as an alternative promoter, which might be of potential interest, was studied. Some papers claim that Zn may even be superior to Ga. These Zn/ZSM-5 zeolites appear to be highly selective in converting ethylene into aromatics at atmospheric pressure and temperatures of 400-500°C making it worthwhile to discuss Zn in some more detail.

4.1.1 Main Findings

- In the aromatization of dilute ethylene Zn/ZSM-5 catalyst is a potential alternative to Ga/ZSM-5.
- Both the zeolitic protons and the Zn promoter co-operate as active sites, each responsible for a different sequence of reactions.
- The active metal site for aromatization very likely is cationic Zn at an ion-exchange position. Small ZnO clusters only catalyse dehydrogenation reactions but do not catalyse aromatization.
- As Zn at an ion-exchange position eliminates a zeolitic proton which is an essential active site, a suitable balance between the metallic and acidic functions is required. Thus the Zn/H^+ ratio or Zn loading is critical.
- A high yield of aromatics was observed using a ZSM-5 catalyst where half the protons were exchanged by Zn ions. Depending on the on the SiO_2/Al_2O_3 ratio, Zn levels should be between 0.4-2 wt% and typically 1 wt% for a ZSM-5 zeolite having a SiO_2/Al_2O_3 ratio of 40.
- Unlike ZnO clusters which are easily reduced and eluted as volatile Zn vapour during operation, Zn ions on an exchange site (the active sites) do not reduce

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[4] Blue Bird TEBE115001 Final Report

under ethylene aromatization conditions and thus the risk of elution of this Zn species is negligible.

- Ion-exchange as a Zn deposition method should lead to catalysts superior to those based on Zn impregnation but Zn levels, and possibly Zn distribution too, depend on exchange conditions, especially contact time.
- Conflicting reports exist on the efficiency of impregnation. It is claimed that on impregnation extra zeolitic ZnO crystals are formed which in contrast to exchanged Zn^{2+} cations, reduce to Zn metal and elute from the catalyst. Only about 54% of the Zn was reported to be present at cation exchange sites, while 46% was present as reducible ZnO crystallites. Others claim 100% Zn dispersion upon impregnation.
- A high-temperature activation step by calcining the dried catalyst at 500°C should be included to promote reaction of Zn species with acidic sites by solid-state ion-exchange, as least for impregnated catalysts.
- Unlike Ga which is deposited as Ga^{3+} and which has to be converted to an active site of lower valency (Ga^{+}) by a reduction/oxidation operation, Zn^{2+} already has the right valency for aromatization and thus no treatment in H_2 should be performed.
- In one study involving a zeolite with a rather high $SiO_2/Al_2O_3 = 71$ the selectivity to aromatics reached a maximum of 64% at 0.74% Zn upon increasing the Zn content. In a different study 1% Zn/ZSM-5 of $SiO_2/Al_2O_3 = 80$ yielded a conversion around 55%.
- In a recent paper on the effect of Ag promotion, the aromatics selectivity of Ag/ZSM-5 was reported to be much higher than that of Ga/ZSM-5 and Zn/ZSM-5.

4.2 Parametric Experimental Study

To obtain more insight into the mechanism of the ethylene aromatization reaction a parametric study was commissioned to the University of Ghent (Belgium). Two different types of catalyst were prepared and were tested with two different gas mixtures. The variables tested were GHSV (Gas Hourly Space Velocity), temperature and pressure. In this section a summary of the results will be given.

4.2.1 Catalysts

Two catalyst samples were studied: a Ga-ZSM5 catalyst, and a Zn-ZSM-5 catalyst. A metal loading of 0.5 wt% was wet impregnated onto the zeolite. The ICP analysis done to the catalysts, however, later showed that the Ga loading only was in the order of 0.2 wt%, considerably lower than expected. The Zn loading of slightly over 0.1 wt% was even lower and thus the results reflect the comparison of 0.2 wt% Ga with 0.1 wt% Zn as promoter. Both samples, physically composed of extrudates of 2 mm diameter and 2-10 mm length, were grinded to a size of 100-200 µm before the tests.

4.2.2 Experimental Conditions

Range of operating conditions: 3, 5 and 10 bar, 300-500°C, 126-189 Nml/min inlet gas.

Due to the pressure drop over the reactor which cannot be ignored, a pressure setpoint below 3 bar is not accurate. Therefore, the experiments at 1 bar could not be performed.

Reference conditions: T = 500°C, p = 5 bar, Flow rate = 126.1 Nml/min (to check the restoration of activity after catalyst regeneration).

Catalyst bed: 100 mg catalyst, diluted with 800 mg α-Al_2O_3 (100-200 µm). Figure 4.1 shows the reactor bed configuration used.

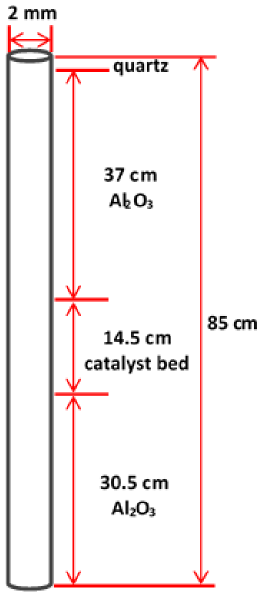

Figure 4.1 Reactor bed configuration. Catalyst size: 100-200 µm. Inert dilute: α-Al2O3, same size as catalyst.

4.2.3 *Main findings*

Ga-ZSM-5 (0.2 wt% Ga) is the best candidate for the aromatics (BTX) production from C_2H_4 in biomass-derived product gas due to its selectivity (up to 16%) and stability. Increasing total pressure leads to a lower conversion of the C_2H_4 which is attributed to fast carbon formation. However, the catalysts can be regenerated by air without loss of initial activity. The presence of H_2 in the gas mixture leads to C_2H_4 hydrogenation and production of C_2H_6. This reaction can be dominant at high H_2/C_2H_4 ratio. Increasing temperature leads to increase of C_2H_4 conversion into BTX but fast catalyst deactivation.

5 Improvement of AREA (BTX Scrubber)

This chapter is devoted to the work performed with AREA (Aromatics Recovery Apparatus) and the steps taken to improve this unit and upscale it to the full content of the generated product gas so that larger samples of bio-BTX can be collected. This work in conjugation with the work performed within the previous “Birds” projects has resulted in a peer reviewed publication:

- Mourao Vilela, C.; Boymans, E.; Vreugdenhil, B. “Co-production of aromatics in biomass and waste gasification”. *Processes*, **2021**, 9, 463.

5.1 AREA 1.0

AREA is an unit dedicated to the selective removal of BTX components from the tar free product gas. Figure 5.1 shows the unit as well as collected BTX samples while Figure 5.2 shows the schematic representation of AREA 1.0 (1 Nm^3/h inlet gas).

Figure 5.1 AREA 1.0 and collected BTX samples

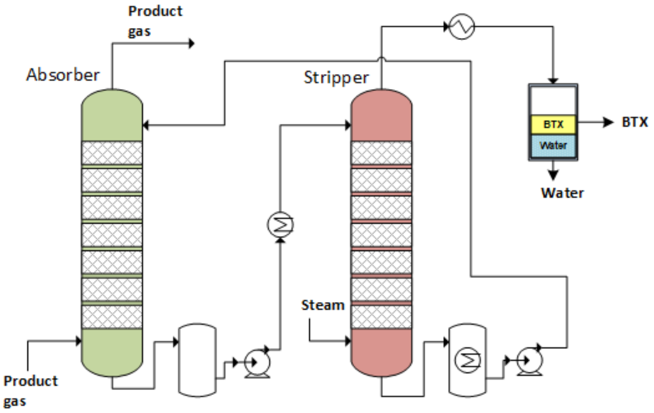

Figure 5.2: Scheme of AREA 1.0

The tar free product gas from MILENA-OLGA enters the absorption column and comes into contact with the silicon oil flowing counter current. The BTX free product gas leaves the absorber and the BTX-rich silicon oil is pumped via a heater to the stripper. Steam is used as the stripping gas and the stripped BTX together with steam enter the cooling system where the full stream condenses. The condensate separates into water and BTX at the automatic separator as shown in Figure 5.3. The regenerated oil is cooled to the absorber temperature and sent back to the absorber. The operating pressure of all the process is atmospheric.

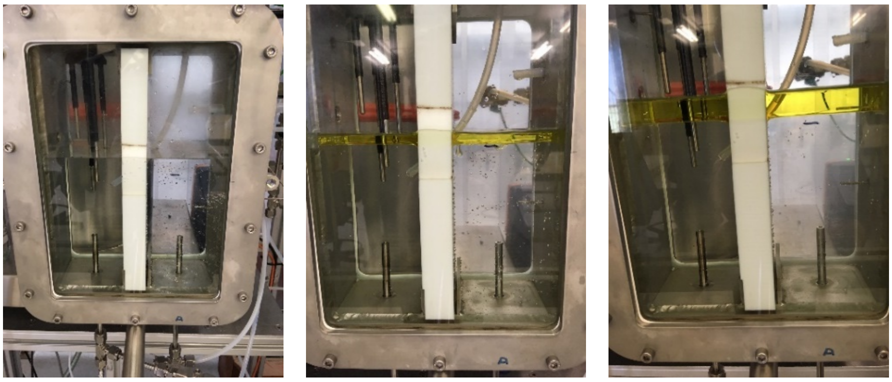

Figure 5.3: Close-ups of the AWOS section where the BTX is automatically separated from water

AREA 1.0 operates at about 98% benzene removal efficiency with an inlet gas flow rate of about 1.0 Nm^3/h, an absorber temperature of 35°C, a stripper temperature of 160°C, with 1.0 Nm^3/h of steam and a liquid absorbent circulation rate of 30 kg/h. These installation temperature and flow settings were applied based on results of early developments and were designed to maximize the harvest of BTX.

Parallel to the installation, also a kinetic absorption model was developed with excel, which allows the prediction of benzene removal performance under different conditions. The experimental results, though limited at the time, were used to fit the mass-transfer-rate expression model. By fitting the rate equation to the experimental data, the model provided the m values, which correspond to the ratio between the concentration of a component in the gas, divided by its concentration in the liquid. However in this early model besides some variation in the stripper gas flow, no other parameters such as temperature or liquid circulation rate were varied in the past for its validation. In the Black Birds project, AREA was modelled using Aspen simulation tool.

Figure 5.4 shows the effect of oil flow rate in the removal of benzene in the product gas based on the Aspen and Excel models. It can be seen that according to the Aspen model the oil flow rate can be further reduced without impacting the benzene removal efficiency.

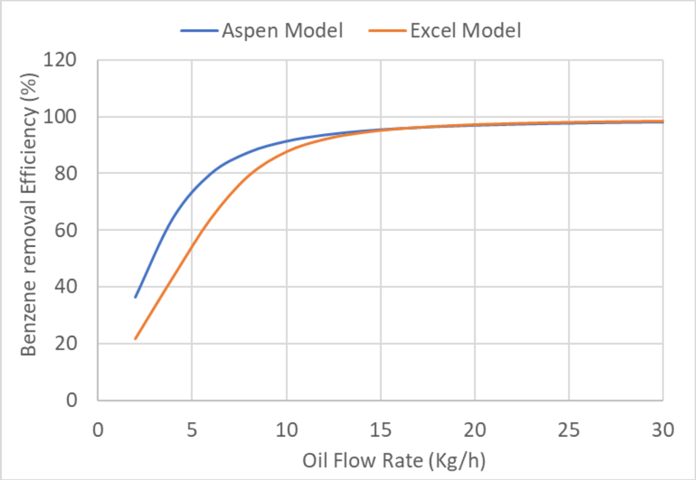

Figure 5.4 Influence of oil flow rate in the benzene removal according to the Aspen and Excel models (all other reference conditions remain unchanged)

To confirm the Aspen model, experiments were carried out at various steam and oil flow rates with the corresponding benzene removal efficiencies measured. The experimental results are shown in Figure 5.5 and Figure 5.6 together with the Aspen and Excel models. The results show a rather good agreement between the model calculations and the experimental results. At low steam (see Figure 5.5) and low oil (see Figure 5.6) flow rates the experimentally observed removal efficiencies are even higher than the calculated values.

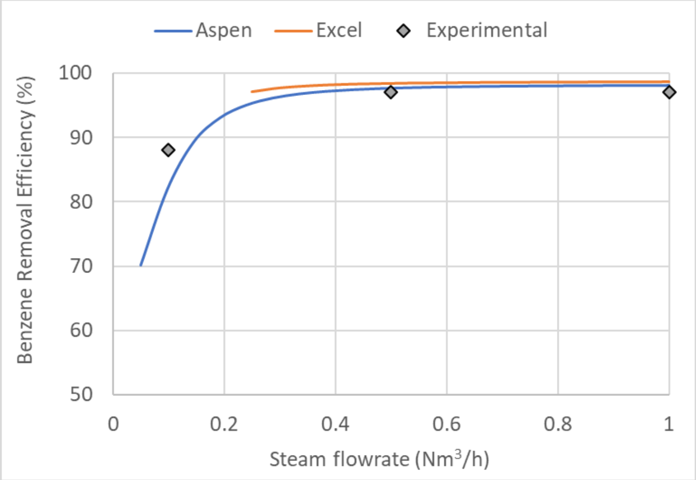

Figure 5.5 Influence of steam flow rate in the benzene removal efficiency (oil flow rate at 30 kg/h, Stripper at 160°C)

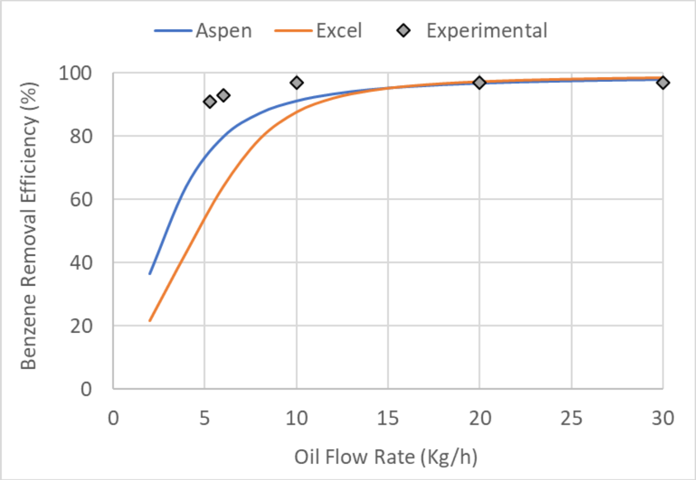

Figure 5.6 Influence of oil flow rate in the benzene removal efficiency (steam flow rate at 1 Nm^3/h, Stripper at 160°C)

This experimental work clearly shows that the flow rates of oil and steam can be further reduced without compromising in great degree the benzene removal efficiency. In fact the benzene removal efficiencies are even higher than those predicted by both models.

5.2 BTX Content

One of the goals of the Black Birds project is to address the quality of the collected BTX product. For this particular task the valuable input by SABIC (and to some extent by CEPSA as well) was crucial. In summary, the BTX could be sent directly to the aromatics train in a chemical refinery; or benzene could be targeted as a product after e.g. distillation. In this section only the collected BTX as a product will be considered. Table 5.1 shows as examples BTX samples collected from gasification processes that have used different types of biobased feedstocks. It is clear that the feedstock used has an impact on the BTX composition.

Table 5.1 Composition of BTX samples collected from the gasification of different biobased feedstocks

BTX samples		*A*	*B*	*C*
Benzene	(wt%)	86	74	59
Toluene	(wt%)	9	11	15
Ethylbenzene	(wt%)	-	1	1
m/p-Xylene	(wt%)	-	-	1
o-Xylene+Styrene	(wt%)	2	5	7

Tar components will also be absorbed in AREA if not removed efficiently by the OLGA tar removal unit. As a consequence these tar components (phenol, naphthalene etc.) will end up in the BTX product and dilute the BTX concentration. OLGA (second loop) is very similar to AREA, i.e. a higher capture of tar will also result in the capture of more BTX in OLGA and therefore a lower overall yield from the BTX. However, the product dilution by tar is not something that needs to be improved at this moment.

5.3 AREA 5.0

During the “Black Birds” project AREA was upscaled to be able to process the full product gas generated in the MILENA gasifier. For the past work a slip-stream of about 1 Nm^3/h was diverted to the AREA (AREA 1.0), and with the upscale AREA (AREA 5.0) will be able to process about 5 Nm^3/h. Hereby much larger quantities of BTX can be collected during the running process. The operating conditions chosen for AREA 5.0 to be used in the feasibility test detailed in Chapter 6 are the following:

- Absorber temperature: 35°C
- Stripper temperature: 130°C
- Oil circulation: 50 kg/h
- Stripper steam: 2 kg/h

6 Feasibility Tests

This chapter is devoted to the demonstration tests performed at bench-scale (25 kW_{th} indirect gasification set-up) to validate the co-production technologies developed under the “Black Birds” project. Lignin A was the feedstock chosen for these testes. Its composition was already shown in Table 2.1. In these tests the upscaled ethylene aromatization unit (DEA) and the upscaled BTX scrubber unit (AREA) were used for the full gas generated in the MILENA gasifier.

The MILENA technology applies indirect gasification where the gasification reactions are separated from the combustion section which is used to provide the necessary heat for the all process. The internal circulation of bed material will ensure the heat transport. The main advantage of this system is that it allows the operation to occur without the use of oxygen (or air) in the gasification process, resulting in a producer gas low in N_2. Figure 6.1 provides the scheme of the 25 kW_{th} MILENA reactor at TNO.

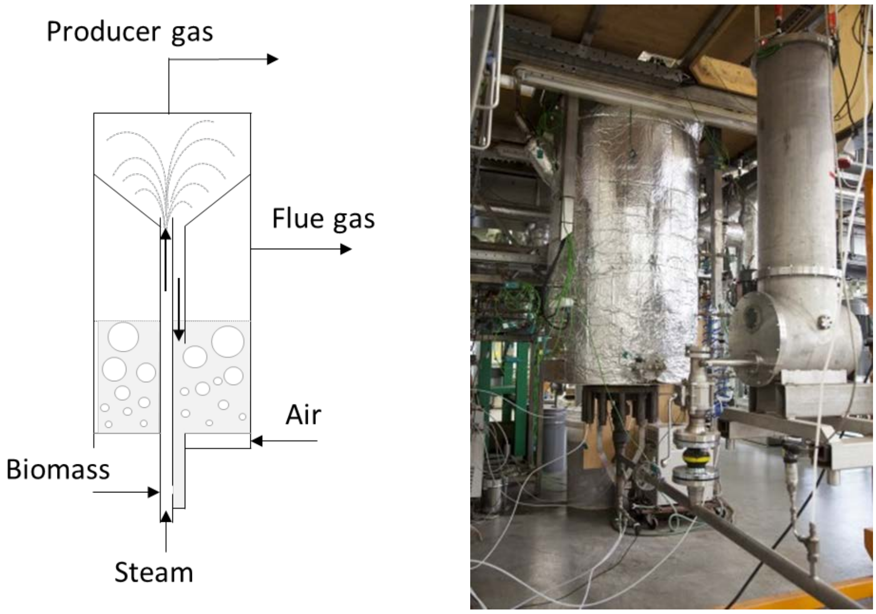

Figure 6.1: Scheme of the MILENA reactor (left) and the lab-scale MILENA (right)

The presence of tar components in the product gas is very challenging due to the deposition of the tar aerosols and heavy tar components in the downstream equipment which demands for maintenance and to additional investment. Another major problem is in the waste water treatment due to the condensation of light tar components. TNO developed its own tar removal technology called OLGA which will remove the tar components from the product gas to a tar dewpoint of less than 10°C. A schematic representation of OLGA is given in the following figure.

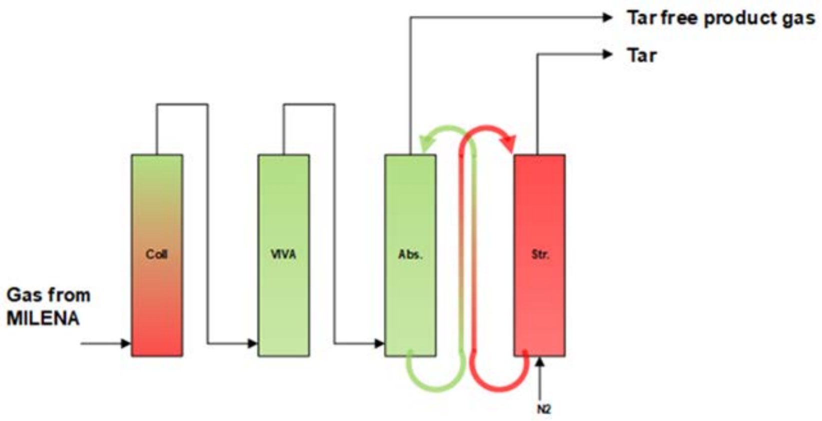

Figure 6.2: OLGA tar removal system at TNO

Two demonstration tests were carried out using 2 different configurations:

1. MILENA – OLGA - DEA (ethylene aromatization) – AREA (BTX scrubber) - ESME for co-production of bio-SNG and aromatics
2. MILENA – OLGA – AREA – Ethylene adsorption

For this work lignin A was chosen as the feedstock, with steam as the carrier gas and olivine as bed material in the MILENA gasifier.

6.1 Configuration 1

This test was performed to validate the concept of co-production of bio-BTX and bio-SNG with ethylene aromatization. Figure 6.3 shows the schematic layout of the experimental set-up. During these tests four micro-GC's in total were placed at different points to observe online the evolution of the product gas composition.

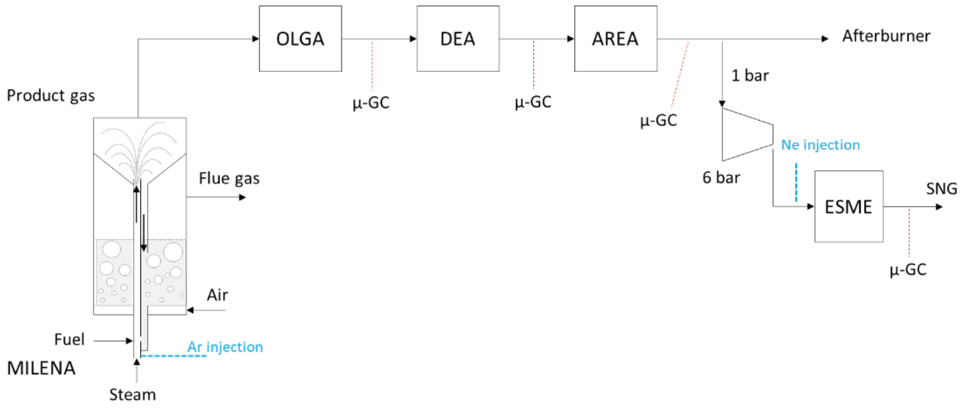

Figure 6.3 Scheme of the experimental set-up for configuration 1

The lignin A is converted into a gas in the MILENA gasifier. The product gas then goes through OLGA so that tars are removed. OLGA is designed to operate above the water dewpoint and to minimize the removal of benzene and toluene. After OLGA the water is condensed and the product gas goes through the ethylene aromatization reactor (DEA) followed by the BTX scrubber unit (AREA) where bio-BTX is collected. After this, a slip stream of about 1 Nm^3/h is diverted, pressurised and sent through ESME with the goal of producing SNG (synthetic natural gas). ESME comprises one guard bed, one HDS reactor and three methanation reactors. The full details of the ESME system can be found in the ECN-E-15-008 report[5].

6.1.1 *Conclusions*

This demonstration test successfully co-produced bio-BTX and bio-SNG with ethylene aromatization via lignin A gasification. With the exception of the DEA all the units operated as expected. BTX was selectively removed from the product gas with 98% efficiency. However the activity of the catalyst used in the DEA was lower than expected and only toluene showed a substantial improvement. For future work it will be important to study in more detail the activity and stability of the catalyst to be used in the ethylene aromatization unit.

The collected bio-BTX was analysed and Figure 6.4 shows the results. It can be seen that benzene and toluene are the largest components and account for about 77% on a mass basis of the collected bio-BTX. If the xylenes and ethylbenzene are also accounted then this value goes to 89% on a mass basis.

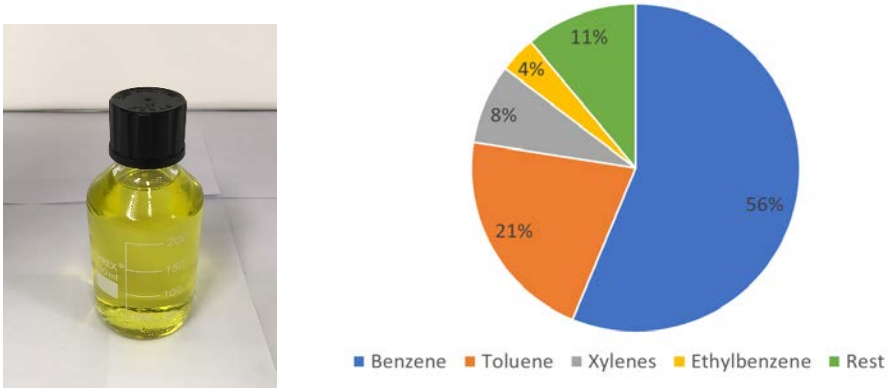

Figure 6.4 Collected bio-BTX (left) and respective analysis on mass basis (right) during Configuration 1 tests

6.2 Configuration 2

This test was performed to validate the concept of ethylene physical adsorption studied by Avantium and detailed in Chapter 3. From the study it was concluded that the BTX should be removed prior the adsorption unit otherwise BTX would be adsorbed as well with ethylene. Another conclusion was that a guard bed of ZnO should be as well present to remove sulphur compounds. Figure 6.5 shows the schematic layout of the experimental set-up. During these tests three micro-GC's in total were placed at different points to observe online the evolution of the product gas composition.

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[5] "500 hours producing bio-SNG from MILENA gasification using the ESME system"; L.P.L.M. Rabou, G. Aranda Almansa; ECN-E-15-008

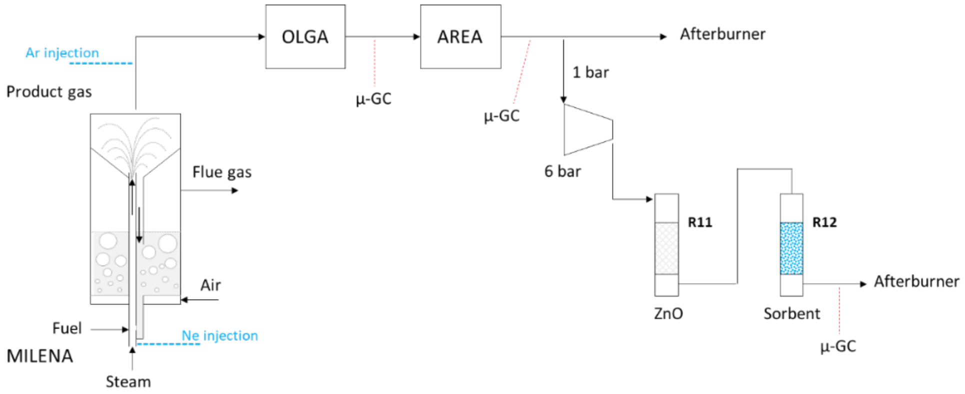


Figure 6.5 Scheme of the experimental set-up for configuration 2

Norit GCN 3070 was the sorbent used in these tests following the conclusions of the study performed by Avantium. Figure 6.6 displays the configuration of the materials and the location of the thermocouples within the reactor R12 which contained the GCN 3070 sorbent. Between two layers of alumina beads, a mixture of 50-50 vol.% alumina and sorbent was placed. The sorbent was mixed with alumina to avoid too sharp temperatures peaks due to strongly exothermal adsorption reaction.

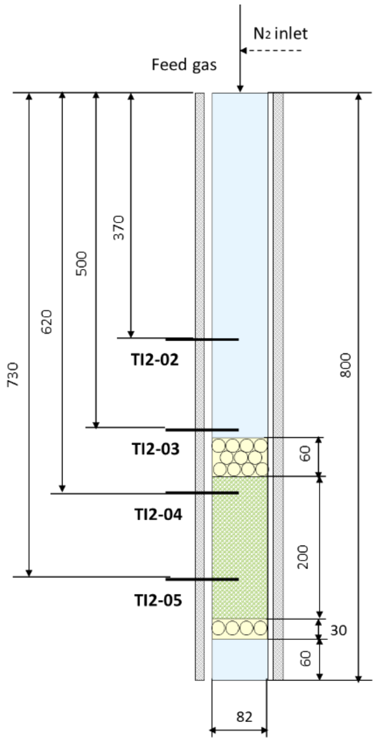


Figure 6.6 Distribution of materials within R12 reactor (all dimensions in mm). Sorbent/alumina bed in green. Yellow layers: alumina beads.

6.2.1 Conclusions

The second demonstration test (Configuration 2) successfully removed ethylene and carbon dioxide selectively from the product gas. However the sorbent reach saturation after about 15 minutes. For future work regeneration techniques should be explored.

7 Application development of the bio-BTX fraction and validation

This chapter will show the work on the application of the bio-BTX collected from the biomass gasification. It will be divided into two sections. The first section, coordinated by Viride, will show the close collaboration with end-users and the market applications and specifications of the bio-BTX. The second section, performed by Kodok, is devoted to a logistics assessment of bio-BTX implementation at a larger scale.

7.1 Application of the Bio-BTX

The application development of the bio-BTX, coordinated by Viride, was performed in close collaboration with end-users. After several discussions two different routes were identified. It may be important to highlight the role of SABIC, which showed interest since the beginning of the project by signing a letter of intent and later joining officially the consortium taking an advisory role. This was considered as a milestone since it shows the potential of the project able to attract the interest of SABIC as a potential end-user. During the project and due to the diligence of Viride, CEPSA was identified as another end-user that showed high interest in the project and its outcome. Based on this, two different applications were identified for the bio-BTX product:

1. Introduce the bio-BTX mixture as it is collected in the aromatics train
2. Bio-benzene could be targeted as a product after e.g. distillation

7.2 Bio-BTX Logistics

In order to get a better understanding of the impact of the combined production of SNG and BTX through wood or lignin gasification on the BTX market and logistics three scenarios are evaluated. To make the comparison between the different scenarios possible, the common factor, the energetic input is kept constant. For all scenarios the energetic input is 82 MW_{th} and is based on the input of the lignin by-product from the DAWN-plant. For all scenarios it is assumed that the gasification is combined with SNG production, ethylene aromatization and subsequent BTX scrubbing. The used gasification-, SNG- and BTX-data are from TNO.

The following scenarios were selected for evaluation:

- Scenario 1: Small scale wood chips gasification with transport of the BTX to a central location for further processing (chemical plant).
- Scenario 2: Large scale wood pellet gasification close to BTX application site.
- Scenario 3: Lignin gasification scaled to the production of lignin as by-product of the DAWN process of Avantium. The gasifier is located next to the DAWN installation.

7.2.1 Scenario 1: Small scale wood gasification with transport of the BTX to central location

In scenario 1, showcased in Figure 7.1, a network of smaller gasifiers is foreseen which are fuelled with local available wood chips. The logistics of the fuel determines the optimal capacity of the gasifier. In this scenario the biomass transport distances are minimized. As a consequence, per gasifier, a relative small amount of BTX is produced. Therefore, transport of the BTX product from the individual gasifiers to a central BTX processing location is taken into account. The capacity of each gasifier is set at 5.2 MW_{th}, so in total a network of ca. 16 gasifiers adds up to a total fuel input of 82 MW_{th}.

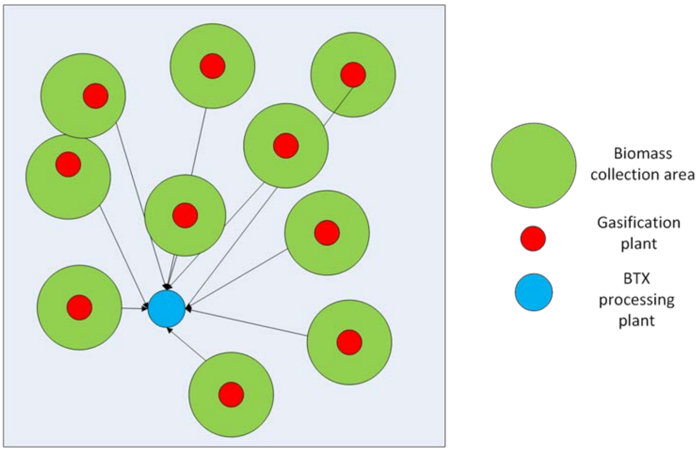


Figure 7.1 Schematics of scenario 1

7.2.2 *Scenario 2: Large scale wood gasification close to BTX application site*

Scenario 2, Figure 7.2, is ideally situated in a harbour area and at the same time close to a BTX end-user. The BTX transport distance is minimized in this scenario. As the biomass volume needed (in the form of wood pellets) is substantial, transport of the fuel per ship to the gasifier is used as base case. The optimal capacity of the gasifier is determined either by biomass fuel- or BTX logistics. In order to make the comparison between the different scenarios possible the fuel input is set at 82 MW_{th}. As the gasifier is located adjacent to the BTX processing plant the BTX is transported by pipeline from the gasification plant to the BTX processing plant.

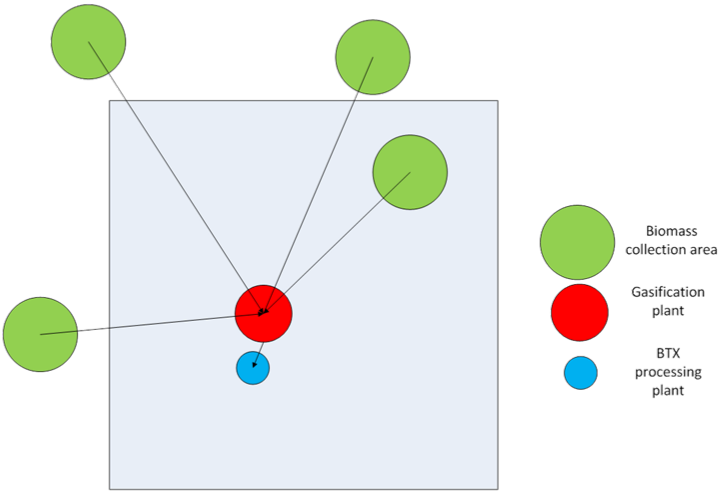


Figure 7.2 Schematics of scenario 2

7.2.3 *Scenario 3: Lignin gasification scaled to the production of lignin through the DAWN process of Avantium*

In the scenario 3, Figure 7.3, the gasifier is situated next to the biorefinery plant (DAWN process of Avantium) in order to minimize transport costs of the lignin, which serves as fuel for the gasifier. The foreseen DAWN plant has an output of lignin of 100 kton/yr with a calorific value of 23,6 MJ/kg. The energetic input of the lignin gasifier with 8.000 operational hours is then 82 MW_{th}.

All lignin, being a side-product from the DAWN technology, is used for the adjacent gasifier. Information on the gas and/or heat demand of the DAWN process is not available so the option to use SNG and/or heat from the gasification plant as utility for the DAWN process is not taken into account.

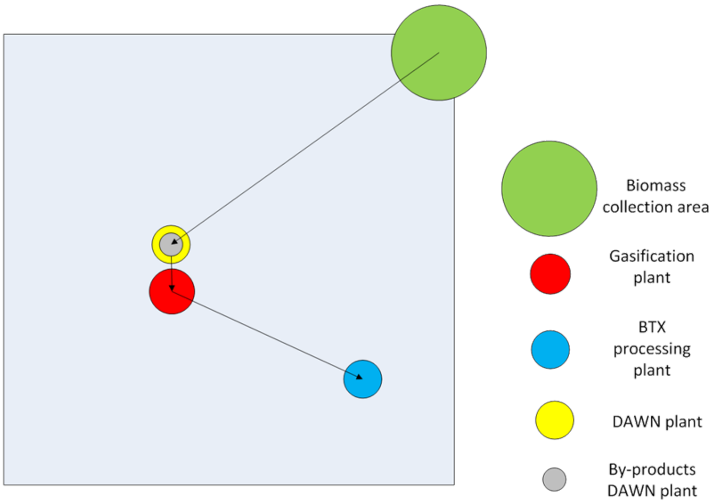


Figure 7.3 Schematics of scenario 3

7.2.4 Assumptions

For all scenarios the produced SNG is either injected into the existing gas grid or supplied to a (larger) gas consumer such as an industrial production site or a district heating installation. At present it is not clear whether the integral process (gasification including BTX production and ethylene aromatization) also produces excess heat. The following assumptions were made:

- Transport of wood (pellets or chips) and BTX per truck, train or ship
- Wood is supplied in the form of wood pellets (scenario 2) or in the case of smaller gasifiers (scenario 1) wood chips
- Main product of the gasification is SNG which is either injected in the gas grid or delivered directly to (large) gas consumers
- The location of the gasifier is situated next to a SNG input into a gas grid entry point or next to a (large) gas consumer
- BTX production includes ethylene aromatization

Table 7.1 shows the data used for the calculations.

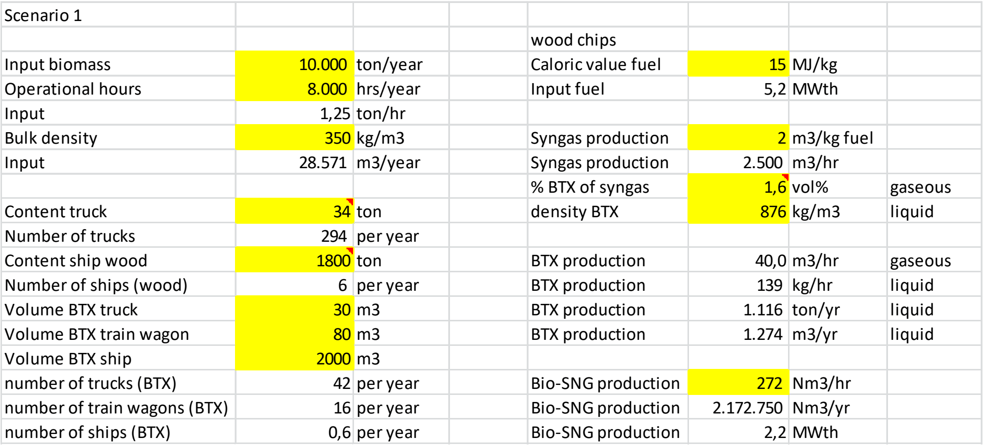
Table 7.1 Data used for the calculation for different scenarios

	Unit	Value	Remarks
Bulk density wood (dried)	kg/m^3	600	Wood pellets
Bulk density wood (dried)	kg/m^3	350	Wood chips
Bulk density lignin	kg/m^3	800	
Caloric value wood	MJ/kg (LHV)	18	Wood pellets
Caloric value wood	MJ/kg (LHV)	15	Wood chips
Caloric value lignin	MJ/kg (LHV)	23,6	Information from TNO
Bulk density BTX (liquid)	kg/m^3	876	
Volume wood truck	ton	34	From reference[6]
Volume wood ship	ton	1.800	From reference[7]
Volume BTX truck	m^3	30	
Volume BTX ship	m^3	2.000	
Volume BTX train wagon	m^3	80	From reference[8]
Operational hours gasifier	hrs/yr	8.000	Similar to data used by TNO
BTX production (4 MW$_{th}$)	kg/hr	63,41	Based on 4 MW$_{th}$ input, source Aspen calculation TNO
SNG production (4 MW$_{th}$)	m^3/hr	222,84	Based on 4 MW$_{th}$ input, source Aspen calculation TNO
CH_4 content SNG	vol%	88,6	Based on 4 MW$_{th}$ input, source Aspen calculation TNO

7.2.5 Results

Table 7.2 shows the results for scenario 1 for one of the small gasifiers while Table 7.3 shows the overall results for the total of 16 small gasifiers. It can be seen that to match the overall energetic input of 82 MWth ca. 16 small scale gasifiers of each 5,2 MWth are necessary.

Table 7.2 Results for scenario 1. Small scale wood gasification with wood chips (one installation)



Scenario 1							
				wood chips			
Input biomass	10.000	ton/year		Caloric value fuel	15	MJ/kg	
Operational hours	8.000	hrs/year		Input fuel	5,2	MWth	
Input	1,25	ton/hr					
Bulk density	350	kg/m3		Syngas production	2	m3/kg fuel	
Input	28.571	m3/year		Syngas production	2.500	m3/hr	
				% BTX of syngas	1,6	vol%	gaseous
Content truck	34	ton		density BTX	876	kg/m3	liquid
Number of trucks	294	per year					
Content ship wood	1800	ton		BTX production	40,0	m3/hr	gaseous
Number of ships (wood)	6	per year		BTX production	139	kg/hr	liquid
Volume BTX truck	30	m3		BTX production	1.116	ton/yr	liquid
Volume BTX train wagon	80	m3		BTX production	1.274	m3/yr	liquid
Volume BTX ship	2000	m3					
number of trucks (BTX)	42	per year		Bio-SNG production	272	Nm3/hr	
number of train wagons (BTX)	16	per year		Bio-SNG production	2.172.750	Nm3/yr	
number of ships (BTX)	0,6	per year		Bio-SNG production	2,2	MWth	

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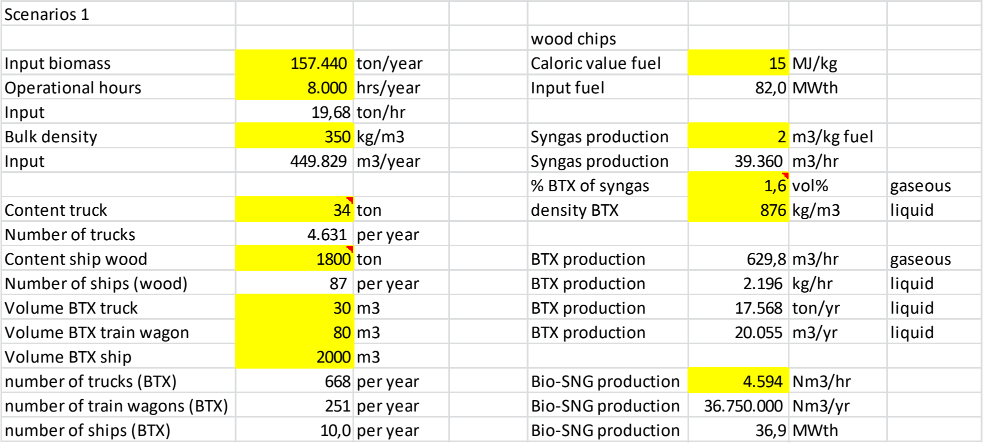
[6] https://ec.europa.eu/energy/intelligent/projects/sites/iee-projects/files/projects/documents/pelletslas_pellet_logistics_data.pdf

[7] https://ec.europa.eu/energy/intelligent/projects/sites/iee-projects/files/projects/documents/pelletslas_pellet_logistics_data.pdf

[8] https://www.vtg.com/wagon-hire/our-fleet/c22080d/

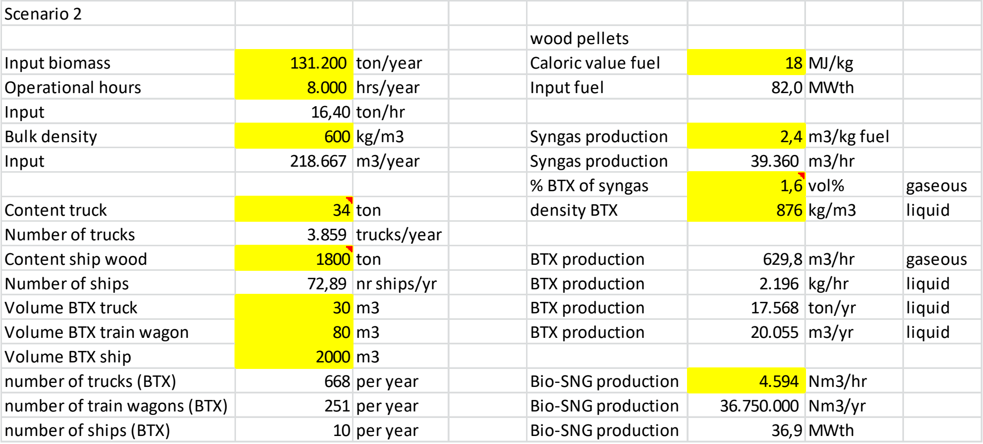
Table 7.3 Results for scenario 1. Small scale wood gasification with wood chips (overall = ca. 16 gasifiers)



Scenarios 1							
				wood chips			
Input biomass	157.440	ton/year		Caloric value fuel	15	MJ/kg	
Operational hours	8.000	hrs/year		Input fuel	82,0	MWth	
Input	19,68	ton/hr					
Bulk density	350	kg/m3		Syngas production	2	m3/kg fuel	
Input	449.829	m3/year		Syngas production	39.360	m3/hr	
				% BTX of syngas	1,6	vol%	gaseous
Content truck	34	ton		density BTX	876	kg/m3	liquid
Number of trucks	4.631	per year					
Content ship wood	1800	ton		BTX production	629,8	m3/hr	gaseous
Number of ships (wood)	87	per year		BTX production	2.196	kg/hr	liquid
Volume BTX truck	30	m3		BTX production	17.568	ton/yr	liquid
Volume BTX train wagon	80	m3		BTX production	20.055	m3/yr	liquid
Volume BTX ship	2000	m3					
number of trucks (BTX)	668	per year		Bio-SNG production	4.594	Nm3/hr	
number of train wagons (BTX)	251	per year		Bio-SNG production	36.750.000	Nm3/yr	
number of ships (BTX)	10,0	per year		Bio-SNG production	36,9	MWth	

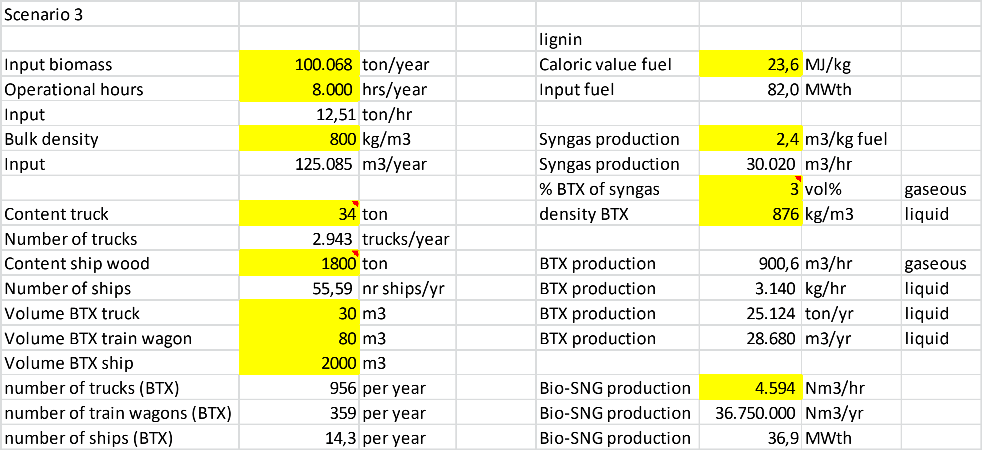
Table 7.4 shows the results for scenario 2 while Table 7.5 shows the results for scenario 3.

Table 7.4 Results for scenario 2. Large scale wood gasification with wood pellets



Scenario 2							
				wood pellets			
Input biomass	131.200	ton/year		Caloric value fuel	18	MJ/kg	
Operational hours	8.000	hrs/year		Input fuel	82,0	MWth	
Input	16,40	ton/hr					
Bulk density	600	kg/m3		Syngas production	2,4	m3/kg fuel	
Input	218.667	m3/year		Syngas production	39.360	m3/hr	
				% BTX of syngas	1,6	vol%	gaseous
Content truck	34	ton		density BTX	876	kg/m3	liquid
Number of trucks	3.859	trucks/year					
Content ship wood	1800	ton		BTX production	629,8	m3/hr	gaseous
Number of ships	72,89	nr ships/yr		BTX production	2.196	kg/hr	liquid
Volume BTX truck	30	m3		BTX production	17.568	ton/yr	liquid
Volume BTX train wagon	80	m3		BTX production	20.055	m3/yr	liquid
Volume BTX ship	2000	m3					
number of trucks (BTX)	668	per year		Bio-SNG production	4.594	Nm3/hr	
number of train wagons (BTX)	251	per year		Bio-SNG production	36.750.000	Nm3/yr	
number of ships (BTX)	10	per year		Bio-SNG production	36,9	MWth	

Table 7.5 Results for scenario 3. Lignin gasification next to DAWN process plant



Scenario 3							
				lignin			
Input biomass	100.068	ton/year		Caloric value fuel	23,6	MJ/kg	
Operational hours	8.000	hrs/year		Input fuel	82,0	MWth	
Input	12,51	ton/hr					
Bulk density	800	kg/m3		Syngas production	2,4	m3/kg fuel	
Input	125.085	m3/year		Syngas production	30.020	m3/hr	
				% BTX of syngas	3	vol%	gaseous
Content truck	34	ton		density BTX	876	kg/m3	liquid
Number of trucks	2.943	trucks/year					
Content ship wood	1800	ton		BTX production	900,6	m3/hr	gaseous
Number of ships	55,59	nr ships/yr		BTX production	3.140	kg/hr	liquid
Volume BTX truck	30	m3		BTX production	25.124	ton/yr	liquid
Volume BTX train wagon	80	m3		BTX production	28.680	m3/yr	liquid
Volume BTX ship	2000	m3					
number of trucks (BTX)	956	per year		Bio-SNG production	4.594	Nm3/hr	
number of train wagons (BTX)	359	per year		Bio-SNG production	36.750.000	Nm3/yr	
number of ships (BTX)	14,3	per year		Bio-SNG production	36,9	MWth	

Figure 7.4 Scenario 3: Lignin gasification next to DAWN process plant

- The amount of surplus heat from the gasification process is still to be determined. At present these data are not yet available. This might have an influence on the selection of the optimal location (for instance a location adjacent to a heat consuming activity such as district heating system or a chemical plant). Examples of district heating are the Rotterdam Warmte bedrijf (capacity 105 MW_{th}) or Biowarmte centrale Purmerend (capacity 44 MW_{th}).
- For the present calculations assumptions are made concerning higher BTX yield from lignin gasification.

7.2.6 Conclusions

- At the scale used in the three scenario's the production of bio-SNG is 36,750,000 Nm^3/year and simultaneously 20,055 m^3 for scenario's 1 and 2 and 28,680 m^3 for scenario 3 of bio-BTX are produced.
- The selection for the optimal scenario is determined by either the logistics (biomass transport movements versus bio-BTX transport either by truck/train or pipe line) with the accompanying environmental en safety issues. Furthermore, the possibility of heat supply to third parties will have an impact on the overall energetic efficiency and financial feasibility.
- The total bio-BTX production corresponds to a limited fraction of the present worldwide fossil fuel based BTX production.

8 Techno-Economic Evaluation

The Techno-Economic Evaluation was part of a PDEng final year assignment from the TU Eindhoven. Haneef Shijaz, worked for a full year in this task receiving inputs from all the partners. This work resulted in a PDEng thesis:

- Haneef Shijaz; "*Techno- economic Evaluation of the Co- production of Chemicals in the Bio-SNG Process*" PDEng Thesis Number: 2019/071

In this chapter a brief summary is given with focus on the results obtained for each scenario. For more details in the modelling and methodology applied the reader is referred to the PDEng thesis.

8.1 Introduction

Natural gas is the main energy source in the Netherlands and its production has fallen deeply due to the associated risk of earthquakes in Groningen caused by the gas production. Meanwhile, concerns about the greenhouse gas emissions from fossil fuels and others are increasing. Substitute natural gas (SNG) is a renewable alternative to the fossil fuel based natural gas since SNG is produced from biomass resulting in net zero emissions. TNO has been developing technologies to produce SNG which meets the Dutch natural gas grid specifications. Hence, SNG can be either directly injected into the grid or mixed with natural gas. In a biomass gasification based process according to TNO, the biomass is first converted in an indirect gasifier (MILENA) into a product gas. This gas contains, besides H_2 and CO (syngas) compounds such as CH_4, C_2-C_4 gases, benzene, toluene and xylene (BTX), and tars. This product gas is sent to the gas cleaning section where dust (in filters and cyclone), tar (tar removal unit named OLGA), sulphur components (hydrodesulphurization and ZnO bed), HCl and water (condenser) are removed. The product gas will also undergo gas conditioning where unsaturated hydrocarbons and (remaining) aromatics are converted to CO, H_2 and CH_4. This is necessary to prevent the carbon soot formation and the resulting deactivation of the downstream nickel based methanation catalyst. The cleaned and conditioned product gas is then converted into SNG by catalytic methanation to achieve grid specification after downstream water and CO_2 removal.

Although, the production of SNG is technologically possible, the economic feasibility of the process has to be ensured. Co-production of added value components is a technically feasible step to improve the profitability of this process. Ethylene and BTX present in the product gas have a harmful effect in synthesis processes as coking precursors of catalysts. However, ethylene and BTX have in fact a higher market price excluding subsidies (~17 Euro/GJ) than the methane product (~ 5 Euro/GJ)[9]. Therefore the co-production of ethylene and BTX in the SNG process would improve its economic potential and on the other hand, avoid their harmful effects of catalyst deactivation in the process. Although the technology for separating ethylene from the product gas is yet at the research phase, it can be converted to BTX via catalytic aromatization process. Hereby this study investigates the techno-economic feasibility of the co-production of BTX and ethylene in the biomass gasification based SNG process.

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[9] ICIS Chemical Business, 7-13 March 2016

The main objective of this work is to carry out the techno-economic evaluation of the following scenarios based on the CAPEX and OPEX values. The chosen scenarios are as follows:

1. Bio-SNG production via wood gasification and product gas conversion to SNG
2. Bio-SNG production via wood gasification with bio-BTX co-production via separation from the product gas
3. Bio-SNG production via wood gasification with bio-BTX co-production via ethylene aromatization and subsequent separation from the product gas
4. Bio-SNG production via wood gasification with bio-BTX and ethylene co-production via separation from the product gas
5. Bio-SNG production via wood gasification with BTX co-production via aromatization of the separated ethylene from the product gas and subsequent separation of BTX
6. Bio-SNG production with the co-production of BTX and /or ethylene from the lignin feedstock for the best wood gasification based scenario.

8.2 Methodology

8.2.1 Capacity

The plant capacity has been decided based on the maximum availability of the feedstock lignin for the final scenario and its energy value. The maximum available lignin is 100 ktons/year with an energy value of 23.6 MJ/kg. The annual operating hours is fixed as 8000 h (91% availability). Therefore, 82 MW of thermal energy in the biomass feed is the energy input of all the scenarios.

8.2.2 Modelling the process scenarios

All the process scenarios are modelled using Aspen Plus with the exception of the MILENA gasifier. The OLGA and BioBTX models developed during this work are integrated. The input gas composition is obtained from experimental data.

8.2.3 Economic Evaluation

The capital and the operating costs of all the proposed process scenarios are evaluated to select the bio-SNG production process of the highest economic potential among them. In general, cost evaluations are done for various purposes and the methods applied are summarised in Table 8.1 . These methods are classified based on the details required for the evaluation, the accuracy and the corresponding applications.

Table 8.1 Classification of the capital cost estimation methods[10]

Estimate	Details needed	Accuracy	Duration	Application
Order of Magnitude	Method of Hill, 1956. Production rate and PFD with compressors, reactors and separation equipment. Based on similar plants	-30 to +50	Very Fast	Profitability analysis
Study	Overall factor method of Lang,1947. Mass and energy balance and equipment sizing	-25 to +30	Fast	Preliminary design
Preliminary	Individual factors method of Guthrie, 1969,1974. Mass and energy balance, equipment sizing, construction materials and P&ID. Enough data to budget estimation	-20 to +25	Medium	Budget approval
Definitive	Full data but before drawings and specifications	-10 to +15	Slow	Construction control
Detailed	Detailed Engineering	-5 to +10	Very slow	Turnkey contract

In this work, the study estimation has been used and the mass and energy balances and equipment specifications have been used. Instead of the overall Lang factor, the individual distribution factors are used to account for the elements of CAPEX and OPEX.

8.2.3.1 *Elements of CAPEX and OPEX*

The guidelines of the Association for the Advancement of Cost Estimating (AACE) were used for the economic evaluation[11]. The main elements of the CAPEX and OPEX are given in Table 8.2 and Table 8.3. The CAPEX includes the cost associated with the construction of the plant which is ready for the operation at the designed capacity. The OPEX stands for the cost related to the normal operation of the plant and is usually expressed on annual basis. The total capital requirements are evaluated based on the purchase equipment costs and applying factors for: handling and setting; commodity material and labour costs; field indirect engineering; overhead and administration; contingencies.

Table 8.2 Elements of CAPEX

Cost Element	**Description**	**Calculation**
Bare purchase equipment cost	Cost associated with the purchasing and transporting the equipment to the plant site.	From quotations, previous project equipment cost, published equipment cost, scale up of data for similar equipment of other capacities.
Handling and placing	Cost of unloading and placing the equipment in its spot at plant site	Using factors as a percentage of delivered equipment cost

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[10] Green.D.W, Perry.R.H, Perry's chemical engineer's handbook, 8th edition (2007)

[11] Conducting technical and economic evaluations- as applied for the process and utility industries. AACE international recommended practice no.16R-90

Direct Cost	Material and labour cost associated with the installation of equipment	Using factors as a percentage of the bare equipment cost
Foundations Structures Buildings Insulation Instruments Electrical Piping Painting Miscellaneous	These are the nine bulk items considered in the installation of equipment.	Material and labour costs are calculated for each using the factors (based on type of components and operating conditions) as a percentage of bare equipment cost. (Material cost as a percentage of bare equipment cost and labour cost as a percentage of material cost)
Indirect cost	Costs which are not the part of the installation but which are required for the orderly completion of the installation.	As a function of direct field labour cost
Total process capital	It is the sum of direct and indirect cost of the installation	From the direct and indirect costs of installation
General Facilities	These include roads, fences, shops, laboratories, office buildings etc.	As a fraction of total process capital
Home office, overhead and fee	The supervision and the office	As a fraction of total process capital
Process contingency	Unforeseen costs and expected omissions due the lack of complete engineering	As a fraction of total process capital based on the state of technology development
Project contingency	Unforeseen costs in project management	As a fraction of process capital plus home office overhead and fees plus process contingencies.
Prepaid royalties		Percentage of total process capital
Start-up costs	Costs for the plant start-up such as operator training, extra maintenance, plant modifications and insufficient operation	One month of total annual operating cost
Working capital	Working capital is needed to maintain the very day needs of operating the plant..	Two months of total annual operating cost
Spare parts		Percentage of total plant cost
Initial catalyst and chemicals		Calculate separately
Land		Calculate separately

Table 8.3 Elements of OPEX

Cost Element	Description	Calculation
Raw materials less by products	Cost of raw material required (per year) minus the annual product sales of by products	Use the cost from market data and the flow rates from the flowsheet
Utilities and chemicals	Cost of utilities and chemicals for each unit	Use the cost from price data and demand from the flowsheet
Direct operating labour	Annual operator charges for the operation of the plant	Calculated from the number of shifts, workers/shift, annual working hours and labour changes
Maintenance, Supervision and overhead, etc.		As a function of direct operating labour

The results from the Aspen models have been used for the economic evaluation of the scenarios. The process has been divided into sub-sections based on the type of components handling, operating conditions and the industrial maturity of the corresponding sections. This helps in applying reasonable cost factors for each of them. The purchase cost for the equipment is the base for the economic evaluations and therefore the elements of the cost will be calculated by applying the distribution factors in the purchase cost. For the evaluation of the purchase cost, the equipment's need to be sized and this equipment sizing was done via a rough engineering approach.

8.2.3.2 *Assumptions*

- The production availability is 91% which is equal to 8000 hours/year operation
- Plant economic life is 20 years
- Overnight construction is assumed which means that the whole CAPEX will be spent in the first year
- Time value of the money is not considered
- Two years are required for reaching the design capacity of the plant (this was used for the calculation of the working capital)

8.2.3.3 *Profitability analysis*

The following criteria are used to indicate the profitability of the process.

1 Pay-out time (POT)

It is used when a one-time investment generates a year after year cash flow and is defined as

$$\text{POT} = \frac{Io}{CF}$$

For a process industry, projects with a POT of 3 years or more are unattractive. For energy industry this term is higher

2 Return on Investment (ROI)

It is the reciprocal of the POT and is defined as the cash flow return of each year

$$\text{ROI} = \frac{CF}{Io}$$

3 Internal Rate of Return (IRR)

IRR is the annual rate at which the investment can be regained for a constant yearly cash flow. If the ROI is negative IRR is not calculated.

$$\mathrm{Io} = CF * \frac{(1+i)^{n}-1}{(1+i)^{n} * i}$$

CF- Cash flow per year
Io- One time investment (CAPEX)
i- Annual interest rate (IRR)

8.3 Conclusions

- At market prices the co-production of bio-BTX improves the revenues of the SNG production by 30 % for scenario 2 and 60% for scenario 3
- At fossil based market prices, the profitability of all scenarios is not interesting
- Considering the currently available incentives for bio-SNG the profitability of all the scenarios is interesting. However since the subsidized SNG selling price is higher than the non-subsidized bio-BTX the co-production leads to a reduction in the profitability.
- Bio-BTX must have incentives of at least twice the market price to lead to an improvement of the profitability of co-production scenarios as compared to the reference case considering the subsidized price of bio-SNG at 1.05 €/kg.
- Current market price of CO_2 of 29 €/ton is not enough to improve the profitability of the scenarios to an interesting level
- CO_2 avoided from BTX application is the second biggest contribution following that of SNG usage in CO_2 avoided incentives
- CO_2 values of 150 €/kg provide an ROI of 10% for scenario 3.
- The minimum SNG price required to achieve an IRR of 10 is for scenario 1 of 0.8 and 0.73 for scenarios with and without CO_2 incentives respectively
- A reduction by half in the adsorption capacity of ethylene would result in an increase of 4% in CAPEX
- Lignin gives a better profitability than wood chips as feedstock as long as it costs less than 30 €/ton without incentives on SNG and less than 8 €/ton with incentives on SNG.

9 Conclusions & Outlook

9.1 Conclusions

“Black Birds - Combined thermochemical and catalytic processing adapted for the production of high-value products and energy from lignin” is a TKI project financed by RVO (reference TEBE 117010) that applies the “adaptive radiation” concept to the valorisation of lignin from different biorefinery processes into a portfolio of products with different niche applications. This includes the use of lignin in a combustion process or in the gasification with co-production technologies leading to bio-BTX, bio-ethylene and bio-SNG.

Lignin Y and lignin A were tested under realistic pulverised fuel combustion conditions in the LCS (lab-scale combustion simulator) at TNO. It could be demonstrated that neither significant near-burner slagging nor excessive heat exchanger fouling can be expected from the outcome of the tests. However, in a co-firing scenario with a fuel that contains cations that can react with the chlorine present in the lignin, chloride salt formation is likely to happen which can cause (alkali-) salt induced heat exchanger fouling and potentially high temperature chlorine corrosion. Nitrous oxide formation is not expected to be problematic, provided minimum burner air staging is applied. From an operational point of view, potential corrosion issues appear to form the highest risk when firing lignin A.

The gasification of lignin A in the 5 kW_{th} WOB bubbling fluidized bed gasifier leads to lower amounts of product gas (and as consequence larger amounts of char) though it also leads to similar values of ethylene, benzene and toluene as compared to beechwood gasification (reference material). Gasification at 850°C is preferred over 780°C since it leads to a substantial increase of benzene, toluene and ethylene. Also measures to improve char gasification reactions such as an increase of steam as carrier gas should be taken.

The selective adsorption of ethylene from the product gas was the subject of the study performed by Avantium. Combinations of different zeolites and active carbons were made in order to tune selectivity. In order to enhance ethylene sorption selectivity, different sorbents were combined in layered or mixed beds. The following is concluded:

- None of the tested material can separate alkanes from ethylene.
- Selected activated carbons showed the best selectivity towards ethylene from CO_2.
- Zeolite [Ca]A and carbon GCN-3017 or combinations of these materials are the best options for ethylene adsorption from the product gas.
- For selective CO_2 removal [Na]A or MCM-41 are suitable adsorbents. Specifically, TEPA-treated could be used for better capacity and selectivity at lower pressure.

In a review performed by Catalok, Zn was identified as a potential substitute of Ga in the conversion of ethylene into aromatics. However with the parametric study commissioned to the University of Ghent it was concluded that Ga-ZSM-5 (0.2 wt% Ga) is a better candidate for the aromatics (BTX) production from C_2H_4 as compared to Zn-ZSM-5 (0.1 wt% Zn) due to its selectivity (up to 16%) and stability. Increasing total pressure leads to a lower conversion of the C_2H_4 which is attributed to fast carbon formation. However, the catalysts can be regenerated by air without loss of initial activity.

The BTX scrubber unit (AREA) was modelled using the Aspen simulation tool, which showed that several parameters could be optimized without significant loss of efficiency. Based on this several experiments were performed and the following could be achieved:

- The L/G ratio could be lowered from ~33 kg/Nm^3 to ~11 kg/Nm^3 maintaining 97% benzene capture.
- Steam was lowered from 820 g/h (stripper L/G~24) to 410 g/h maintaining 97% benzene capture.

AREA was upscaled to be able to process the full product gas generated in the MILENA gasifier. For the past work a slip-stream of about 1 Nm^3/h was diverted to the AREA (AREA 1.0), and with the upscale AREA (AREA 5.0) will be able to process about 5 Nm^3/h. The operating conditions are defined based on the work done with AREA 1.0:

- Absorber temperature: 35°C
- Stripper temperature: 130°C
- Oil circulation: 50 kg/h
- Stripper steam: 2 kg/h

The demonstration tests were conducted successfully and proved the feasibility of the co-production technologies developed with the Black Birds project. The first demonstration test (Configuration 1) successfully co-produced bio-BTX and bio-SNG with ethylene aromatization via gasification of lignin. Bio-BTX was selectively removed from the product gas with 98% efficiency. The analysis of the collected sample shows about 85% on mass basis of benzene, toluene and xylenes. However, the activity of the catalyst used in the ethylene aromatization unit (DEA) was lower than expected and mainly toluene was formed. The second demonstration test (Configuration 2) successfully removed ethylene and carbon dioxide selectively from the product gas. However the sorbent reach saturation after about 15 minutes.

The application development of the bio-BTX, coordinated by Viride, was performed in close collaboration with end-users. Two different applications were identified for the bio-BTX product:

- Use it directly as collected in the aromatics train
- Purify the benzene for detergent production

A Techno-Economic Evaluation was performed as part of a PDEng final year assignment from the TU Eindhoven. Some of the main findings can be summarized as follow:

- At market prices the co-production of bio-BTX improves the revenues of the SNG production by 30 % for scenario 2 (SNG with co-production of BTX) and 60% for scenario 3 (SNG with co-production of BTX via ethylene aromatization)
- At fossil based market prices, the business case of all scenarios is negative
- Current market price of CO_2 of 29 €/ton is not enough to make positive business cases for all scenarios
- CO_2 values of 150 €/kg provide an ROI of 10% for scenario 3.

- Lignin gives a better profitability than wood chips as feedstock as long as it costs less than 30 €/ton without incentives on SNG and less than 8 €/ton with incentives on SNG.

9.2 Outlook

This project shows the potential of co-production technologies in the bio-SNG production via biomass gasification. With this work some questions have been answered but others have been opened. Ethylene aromatization is an important step to improve the aromatics present in the product gas as a consequence to improve the yield of the BTX harvested. However in this work the catalyst applied in the demonstration tests was not as active as expected. This is a topic of extreme relevance and that should be studied in more detail in the future. Besides activity, also catalyst stability is important to advance this technology.

The work with selective physical adsorption of ethylene from the product gas was achieved successfully in the demonstration test. However the sorbent reached saturation after about 15 minutes. For future work the regeneration of the sorbent should be studied.

With this project there was a clear development in the market application of the collected bio-BTX. Two different outcomes have been identified and the collected samples have been characterized and compared with market specifications. The next step on the development of these technologies should be to perform a longer demonstration test, about 100 h, with harvesting of bio-BTX that meets market specifications.

The content of chloride (Cl) in the used lignin is problematic.. From an operational point of view, potential corrosion issues appear to form the highest risk when firing or gasifying this feedstock. This may be a point of concern and should be addressed in future work.

10 Dissemination

The activities of the Black Birds project have been released in a number of publications and conference contributions.

10.1 Peer Reviewed Publications

- Mourao Vilela, C.; Boymans, E.; Vreugdenhil, B. “Co-production of aromatics in biomass and waste gasification”. *Processes*, **2021**, 9, 463. https://doi.org/10.3390/pr9030463
- C.M. Lok, J. Van Doorn, G. Aranda Almansa; “Promoted ZSM-5 catalysts for the production of bio-aromatics, a review”; *Renewable and Sustainable Energy Reviews*, **2019**, 113, 109248. https://doi.org/10.1016/j.rser.2019.109248
- Ilona van Zandvoort, Erik-Jan Ras, Robbert de Graaf, Rajamani Krishna; “Using transient breakthrough experiments for screening of adsorbents for separation of C2H4/CO2 mixtures”; *Separation and Purification Technology*, **2020**, 241, 116706. https://doi.org/10.1016/j.seppur.2020.116706
- Ilona van Zandvoort, Jan Kees van der Waal, Erik-Jan Ras, Robbert de Graaf, Rajamani Krishna; “Highlighting non-idealities in C2H4/CO2 mixture adsorption in 5A zeolite”; *Separation and Purification Technology*, **2019**, 227, 115730. https://doi.org/10.1016/j.seppur.2019.115730

10.2 Conferences

- Carlos F. Mourao Vilela, Haneef Shijaz, Evert Boymans, Berend Vreugdenhil; “*Valorisation of the Green Gas route with Bio-BTX co-production*”; EUBCE 2020.
- G. Aranda Almansa; “ Black Birds: Combined thermochemical and catalytic processing adapted for the production of high-value products and energy from lignin”. Circular Convention 14 and 15 March 2018, Geertruidenberg.
- Ilona van Zandvoort; “*Application of humins from sugar dehydration processes*”; ISGC 2019

10.3 Other Contributions

- Black Birds banner and flyers at EUBCE 2019 (Lisbon, Portugal)
- Black Birds banner and flyers at Biorizon 2018 ('s-Hertogenbosch, the Netherlands) and at Biorizon 2019 (Antwerp, Belgium)

11 Signature

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on 23-03-2021

M.H.F. Overwijk
Research Manager

ValidSigned by Carlos Mourao Vilela
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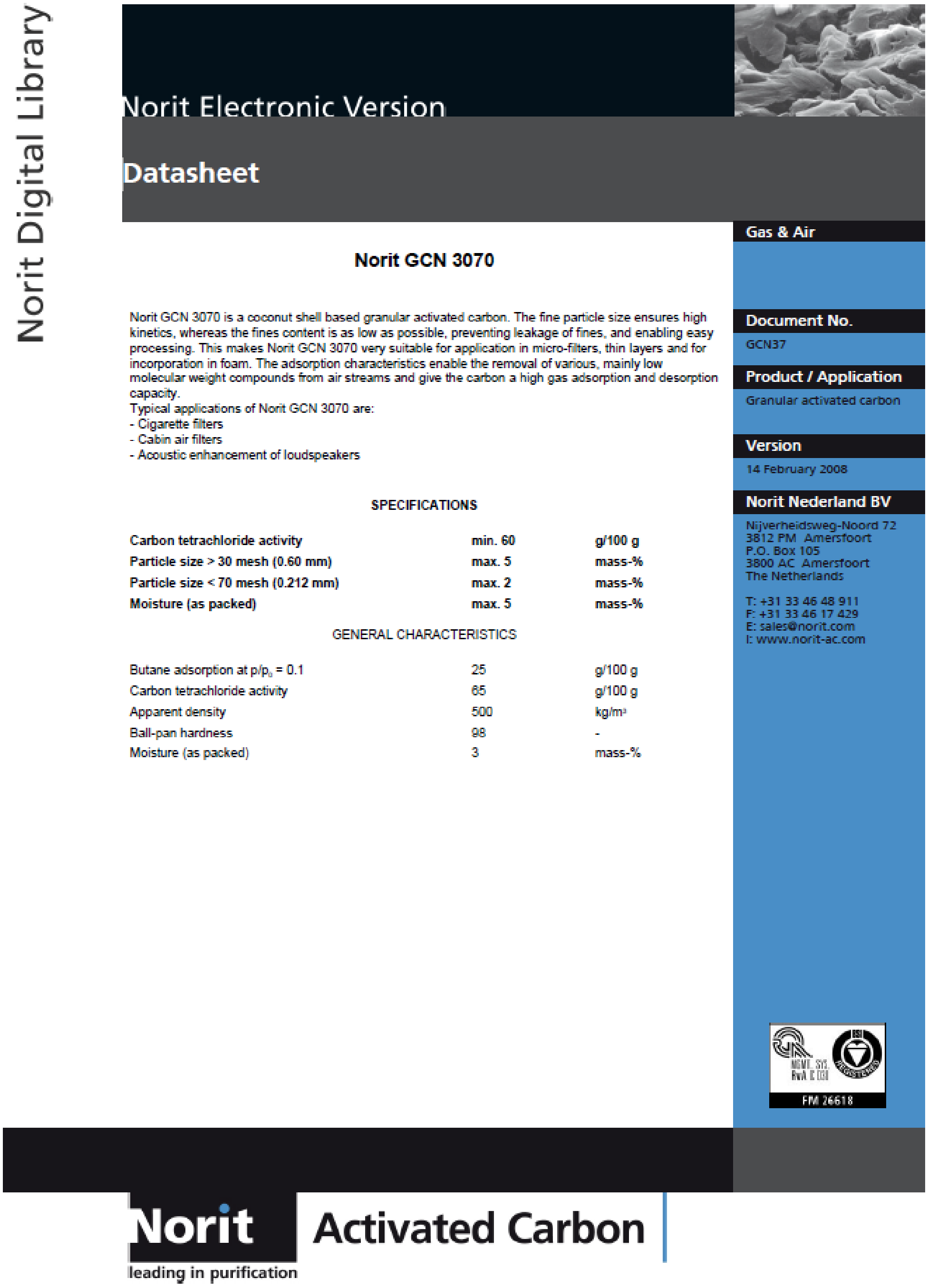
A Norit GCN 3070



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Datasheet

Gas & Air

Norit GCN 3070

Norit GCN 3070 is a coconut shell based granular activated carbon. The fine particle size ensures high kinetics, whereas the fines content is as low as possible, preventing leakage of fines, and enabling easy processing. This makes Norit GCN 3070 very suitable for application in micro-filters, thin layers and for incorporation in foam. The adsorption characteristics enable the removal of various, mainly low molecular weight compounds from air streams and give the carbon a high gas adsorption and desorption capacity.
Typical applications of Norit GCN 3070 are:
- Cigarette filters
- Cabin air filters
- Acoustic enhancement of loudspeakers

SPECIFICATIONS

Carbon tetrachloride activity	**min. 60**	**g/100 g**
Particle size > 30 mesh (0.60 mm)	**max. 5**	**mass-%**
Particle size < 70 mesh (0.212 mm)	**max. 2**	**mass-%**
Moisture (as packed)	**max. 5**	**mass-%**

GENERAL CHARACTERISTICS

Butane adsorption at $p/p_0 = 0.1$	25	g/100 g
Carbon tetrachloride activity	65	g/100 g
Apparent density	500	kg/m^3
Ball-pan hardness	98	-
Moisture (as packed)	3	mass-%

Document No.
GCN37

Product / Application
Granular activated carbon

Version
14 February 2008

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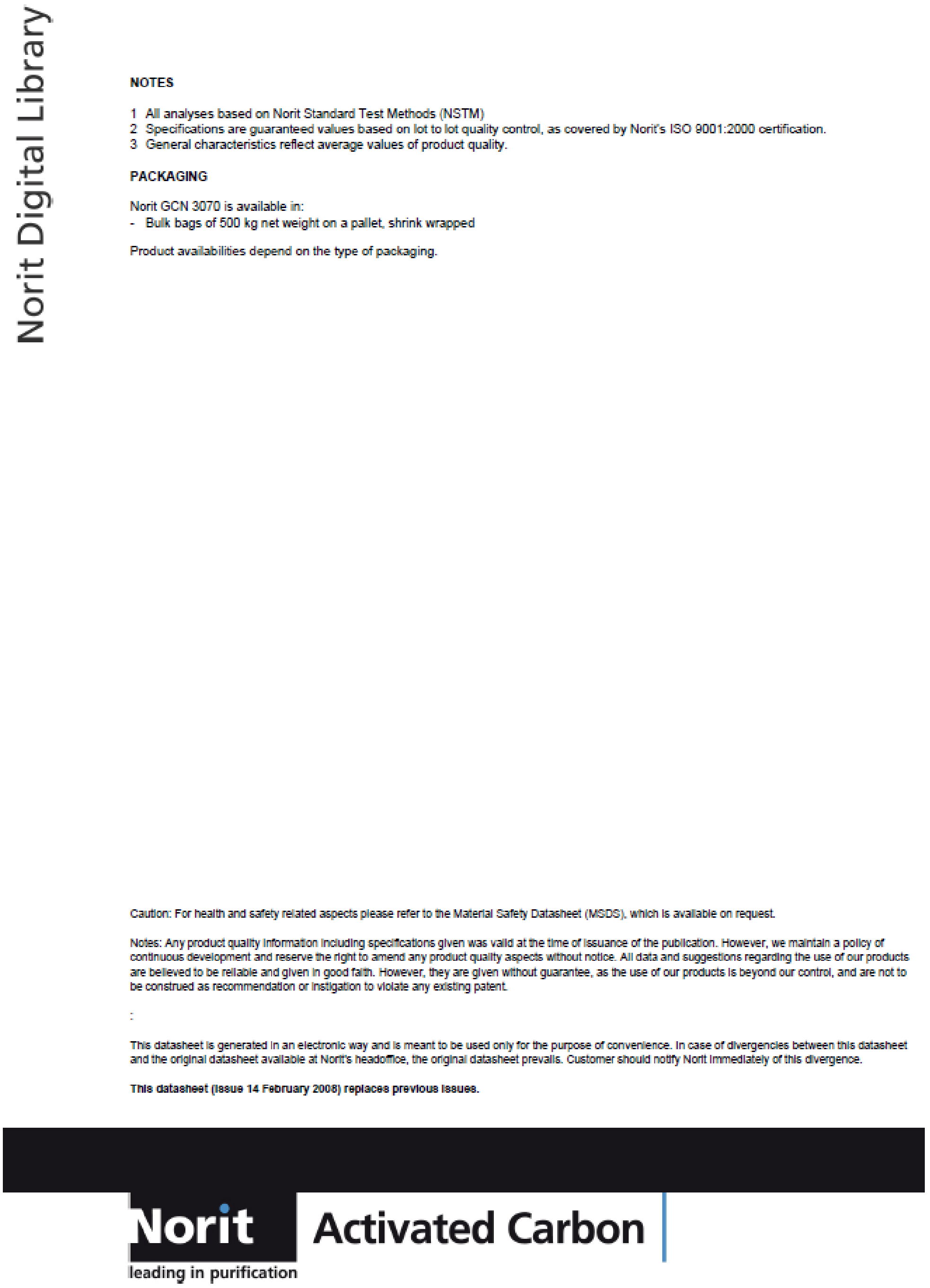

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NOTES

1 All analyses based on Norit Standard Test Methods (NSTM)
2 Specifications are guaranteed values based on lot to lot quality control, as covered by Norit's ISO 9001:2000 certification.
3 General characteristics reflect average values of product quality.

PACKAGING

Norit GCN 3070 is available in:
- Bulk bags of 500 kg net weight on a pallet, shrink wrapped

Product availabilities depend on the type of packaging.

Caution: For health and safety related aspects please refer to the Material Safety Datasheet (MSDS), which is available on request.

Notes: Any product quality information including specifications given was valid at the time of issuance of the publication. However, we maintain a policy of continuous development and reserve the right to amend any product quality aspects without notice. All data and suggestions regarding the use of our products are believed to be reliable and given in good faith. However, they are given without guarantee, as the use of our products is beyond our control, and are not to be construed as recommendation or instigation to violate any existing patent.

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