

Experimental and modelling evaluation of an ammonia-fuelled microchannel reactor for hydrogen generation

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“Life is difficult. This is a great truth, one of the greatest truths. It is a great truth because once we truly see this truth, we transcend it. Once we truly know that life is difficult—once we truly understand and accept it—then life is no longer difficult. Because once it is accepted, the fact that life is difficult no longer matters.”

From “The Road Less Traveled”, book authored by M Scott Peck

“And after you have suffered a little while, the God of all grace, Who has called you to His eternal glory in Christ Jesus, will Himself complete and make you what you ought to be, establish and ground you securely, and strengthen, and settle you.”

1 Peter 5:10

“All men dream but not equally. Those who dream by night in the dusty recesses of their minds wake in the day to find that it was vanity; but the dreamers of the day are dangerous men, for they may act their dream with open eyes to make it possible.”

T.E. Lawrence

“Every great dream begins with a dreamer. Always remember, you have within you the strength, the patience, and the passion to reach for the stars to change the world.”

Harriet Tubman

“Reach high, for stars lie hidden in your soul. Dream deep, for every dream precedes the goal.”

Pamela Vaull Starr

“Our truest life is when we are in dreams awake”

Henry David Thoreau

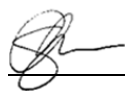
*“So often times it happens that we live our lives in chains
And we never even know we have the key.”*

From “Already Gone”, performed by the Eagles for their 1974 On the Border album.

DECLARATION

I, Steven Chiuta, hereby declare that the thesis entitled: ***“Experimental and modelling evaluation of an ammonia-fuelled microchannel reactor for hydrogen generation”***, submitted in fulfillment of the requirements for the degree *Philosophiae Doctorate* in Chemical Engineering is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution in whole or in part.

Signed at North-West University (Potchefstroom Campus)



Steven Chiuta

20/11/2014

Date

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All the praise and glory is to God, for without Him the completion of this work would not have been possible. In this tremendous journey, I cannot possibly recollect the countless moments that I have witnessed His presence; imparting wonderful ideas in me to levels that I would have otherwise thought inaccessible!!

As I muse over this important instant of my life, I find myself appreciative to several people, without whom I could not have possibly come this far. Foremost, my utmost salutation goes to three extraordinary colleagues who have been influential to the success of this project; Professor Raymond C. Everson (promoter), Professor Hein Neomagus (co-promoter), and Dr. Dmitri G. Bessarabov (co-promoter). These gentlemen extended to me the freedom to “flex my research muscle”, which was imperative and undoubtedly contributed to the success in this well-travelled and worthwhile journey.

Raymond, I have so much good to say, but space limits me and it suffices that your supervision of this research was outright superb: introducing once-a-novice like me to CFD and looking at the success we have had says it all. What will remain engraved in my mind though is your remark when we first met to discuss the way forward, “If it does not have mathematical modelling, I won’t supervise”. Guess what, you were so right!! I am grateful to Hein also, for the many thought-provoking and insightful deliberations that we have had over the years. I grew to appreciate your principle, “Keep it short and to the point”, and it has become second nature. It is probably what succinctly defines the style of this research thesis. I also wish to extend special thanks to Dmitri, for your on-going support in this work, as well as for the opportunity to participate in a field of research that has both been interesting and exciting. Again, thank you for taking your precious time in teaching me all I know about gas chromatography!!

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ABSTRACT

In this thesis, ammonia (NH_3) decomposition was assessed as a fuel processing technology for producing on-demand hydrogen (H_2) for portable and distributed fuel cell applications. This study was motivated by the present lack of infrastructure to generate H_2 for proton exchange membrane (PEM) fuel cells. An overview of past and recent worldwide research activities in the development of reactor technologies for portable and distributed hydrogen generation via NH_3 decomposition was presented in Chapter 2. The objective was to uncover the principal challenges relating to the state-of-the-art in reactor technology and obtain a basis for future improvements. Several important aspects such as reactor design, operability, power generation capacity and efficiency (conversion and energy) were appraised for innovative reactor technologies vis-à-vis microreactors, monolithic reactors, membrane reactors, and electrochemical reactors (electrolyzers). It was observed that substantial research effort is required to progress the innovative reactors to commercialization on a wide basis. The use of integrated experimental-mathematical modelling approach (useful in attaining accurately optimized designs) was notably non-existent for all reactors throughout the surveyed open-literature. Microchannel reactors were however identified as a transformative reactor technology for producing on-demand H_2 for PEM cell applications.

Against this background, miniaturized H_2 production in a stand-alone ammonia-fuelled microchannel reactor (reformer) washcoated with a commercial Ni-Pt/ Al_2O_3 catalyst (ActiSorb[®] O6) was demonstrated successfully in Chapter 3. The reformer performance was evaluated by investigating the effect of reaction temperature (450–700 °C) and gas-hourly-space-velocity (6 520–32 600 $\text{Nml g}_{\text{cat}}^{-1} \text{h}^{-1}$) on key performance parameters including NH_3 conversion, residual NH_3 concentration, H_2 production rate, and pressure drop. Particular attention was devoted to defining operating conditions that minimised residual NH_3 in reformat gas, while producing H_2 at a satisfactory rate. The reformer operated in a daily start-up and shut-down (DSS)-like mode

for a total 750 h comprising of 125 cycles, all to mimic frequent intermittent operation envisaged for fuel cell systems. The reformer exhibited remarkable operation demonstrating 98.7% NH_3 conversion at $32\,600\text{ Nml g}_{\text{cat}}^{-1}\text{ h}^{-1}$ and $700\text{ }^\circ\text{C}$ to generate an estimated fuel cell power output of 5.7 W_e and power density of $16\text{ kW}_e\text{ L}^{-1}$ (based on effective reactor volume). At the same time, reformer operation yielded low pressure drop ($<10\text{ Pa mm}^{-1}$) for all conditions considered. Overall, the microchannel reformer performed sufficiently exceptional to warrant serious consideration in supplying H_2 to low-power fuel cell systems.

In Chapter 4, hydrogen production from the Ni-Pt-washcoated ammonia-fuelled microchannel reactor was mathematically simulated in a three-dimensional (3D) CFD model implemented via Comsol Multiphysics™. The objective was to obtain an understanding of reaction-coupled transport phenomena as well as a fundamental explanation of the observed microchannel reactor performance. The transport processes and reactor performance were elucidated in terms of velocity, temperature, and species concentration distributions, as well as local reaction rate and NH_3 conversion profiles. The baseline case was first investigated to comprehend the behavior of the microchannel reactor, then microstructural design and operating parameters were methodically altered around the baseline conditions to explore the optimum values (case-study optimization).

The modelling results revealed that an optimum NH_3 space velocity (GHSV) of $65.2\text{ NI g}_{\text{cat}}^{-1}\text{ h}^{-1}$ yields 99.1% NH_3 conversion and a power density of $32\text{ kW}_e\text{ L}^{-1}$ at the highest operating temperature of 973 K . It was also shown that a $40\text{-}\mu\text{m}$ -thick porous washcoat was most desirable at these conditions. Finally, a low channel hydraulic diameter ($225\text{ }\mu\text{m}$) was observed to contribute to high NH_3 conversion. Most importantly, mass transport limitations in the porous-washcoat and gas-phase were found to be negligible as depicted by the Damköhler and Fourier numbers, respectively. The experimental microchannel reactor produced 98.2% NH_3 conversion and a power density of $30.8\text{ kW}_e\text{ L}^{-1}$ when tested at the optimum operating conditions

established by the model. Good agreement with experimental data was observed, so the integrated experimental-modeling approach used here may well provide an incisive step toward the efficient design of ammonia-fuelled microchannel reformers.

In Chapter 5, the prospect of producing H_2 via ammonia (NH_3) decomposition was evaluated in an experimental stand-alone microchannel reactor wash-coated with a commercial Cs-promoted Ru/Al_2O_3 catalyst (ACTA Hypermec 10010). The reactor performance was investigated under atmospheric pressure as a function of reaction temperature (723–873 K) and gas-hourly-space-velocity ($65.2\text{--}326.1\text{ NI g}_{cat}^{-1}\text{ h}^{-1}$). Ammonia conversion of 99.8% was demonstrated at $326.1\text{ NI g}_{cat}^{-1}\text{ h}^{-1}$ and 873 K. The H_2 produced at this operating condition was sufficient to yield an estimated fuel cell power output of 60 W_e and power density of $164\text{ kW}_e\text{ L}^{-1}$. Overall, the Ru-based microchannel reactor outperformed other NH_3 microstructured reformers reported in literature including the Ni-based system used in Chapter 3. Furthermore, the microchannel reactor showed a superior performance against a fixed-bed tubular microreactor with the same Ru-based catalyst. Overall, the high H_2 throughput exhibited may promote widespread use of the Ru-based micro-reaction system in high-power applications.

Four peer-reviewed journal publications and six conference publications resulted from this work.

Keywords: ammonia decomposition, microchannel reactor, hydrogen generation, PEM fuel cell, performance evaluation, modelling evaluation

OPSOMMING

In hierdie tesis is die afbreek van ammoniak (NH_3) as brandstof prosesering tegnologie vir die vervaardiging van waterstof (H_2) op aanvraag vir brandstofsel toepassings ondersoek. Hierdie studie is gemotiveer deur die gebrek aan infrastruktuur tans om H_2 te genereer vir proton uitruil membraan (PEM) brandstofselle. 'n Oorsig van huidige en onlangse wêreldwye navorsingsaktiwiteite in die ontwikkeling van reaktor tegnologieë vir skuifbare en verspreide waterstof generasie via NH_3 afbraak is voorgestel in Hoofstuk 2. Die doel is om die hoof uitdagings wat verband hou met die mees moderne reaktor tegnologieë te ontbloot en 'n basis te verkry vir toekomstige verbeterings. Verskeie belangrike aspekte soos reaktor ontwerp, bedryfbaarheid, krag opwekkings kapasiteit en effektiwiteit (omskakeling en energie) is beskou vir baanbrekende reaktor tegnologieë vis-à-vis mikroreaktors, monolitiese reaktors, membraan reaktors en elektrochemiese reaktors (elektroliseerders). Dit is opgemerk dat merkbare navorsings insette nodig is om die baanbrekende reaktors te bevorder tot algemene kommersialisasie. Die gebruik van 'n geïntegreerde eksperimenteel wiskundige modelerings benadering (wat nuttig is om akuraat optimiseerde ontwerpe te verkry) was merkbaar afwesig vir alle reaktors in die literatuur wat beskou is. Mikrokanaal reaktors is identifiseer as 'n transformerende reaktor tegnologie om H_2 op aanvraag te produseer vir PEM sel toepassings.

Met hierdie agtergrond, is 'n verkleinde H_2 vervaardiging in 'n alleenstaande ammoniak gedryfde mikrokanaal reaktor (hervormer) spoelbedek met 'n kommersiële Ni-Pt/ Al_2O_3 katalisator (Actisorb[®] O6) suksesvol gedemonstreer in Hoofstuk 3. Die hervormer se werksverrigting is evalueer deur die ondersoek van die effek van die reaksie temperatuur (450 – 700 °C) en gas uurlikse ruimte snelheid (6.5 – 32.6 $\text{NL g}_{\text{cat}}^{-1} \text{h}^{-1}$) op sleutel prestasie parameters insluitend NH_3 omskakeling, oorblywende NH_3 konsentrasie, H_2 vervaardigings tempo, en drukval. Besondere aandag is geskenk om die bedryfs kondisies wat oorblywende NH_3 in die hervormde gas minimaliseer terwyl H_2 steeds teen 'n bevredigende tempo geproduseer word.

Die hervormer is bedryf soos 'n daaglikse aansluit en afskakel (DSS) modus vir 'n totaal van 750-h wat bestaan uit 125 siklusse, om die dikwels onderbreekte bedryf wat gesien word vir brandstofsels te na-aap. Die hervormer het besonder vertoon tydens operasie deur 98.7% NH_3 om te skakel teen $32.6 \text{ NI g}_{\text{cat}}^{-1} \text{ h}^{-1}$ en 700°C om 'n brandstofsels uitset van ongeveer 5.7 W_e en 'n drywingsdigtheid van $16 \text{ kW}_e \text{ L}^{-1}$ (gebaseer op effektiewe reaktor volume). Terselfdertyd is die drukval tydens hervormer operasie laag ($<10 \text{ Pa mm}^{-1}$) vir alle toestande in ag geneem. Oor die algemeen het die mikrokanaal hervormer uitstekend genoeg presteer om ernstige oorweging te regverdig om H_2 te voorsien vir lae energie brandstofsels stelsels.

In Hoofstuf 4 is die waterstof produksie van die Ni-Pt spoelbedekte ammoniak gedryfde mikrokanaal reaktor wiskundig gesimuleer in 'n driedimensionele (3D) CFD model wat via Comsol Multiphysics™ implimenter is. Die doel is om 'n verstand van die reaksie gekoppelde fenomene te verkry asook 'n fundamentele verduideliking van die waargenome mikrokanaal reaktor se werksverrigting. Die transport prosesse en reaktor uitset is verduidelik in terme van snelheid, temperatuur en spesie konsentrasie verspreidings asook lokale reaksie tempo en NH_3 omskakelings profiele. Die basislyn geval is eers ondersoek om die gedrag van die mikrokanaal reaktor te verstaan en toe is die mikrostrukturele ontwerp en bedryfsparameters metodes verander rondom die grondtoestande om die optimum waardes te ontdek (gevalle studie optimisering).

Die modelerings resultate het ontbloot dat 'n optimum NH_3 ruimte snelheid (GHSV) van $65 \text{ NI g}_{\text{cat}}^{-1} \text{ h}^{-1}$ 99.1% NH_3 omskakeling lewer en 'n drywingsdigtheid van $32 \text{ kW}_e \text{ L}^{-1}$ by die hoogste bedryfs temperatuur van 973 K . Daar is ook gewys dat 'n $40\text{-}\mu\text{m}$ -dik poruese spoelbedekking uiters wenslik is by hierdie toestande. Laastens is waargeneem dat 'n lae kanaal hidroliese deursnit ($225 \mu\text{m}$) lei tot hoë NH_3 omskakeling. Die mees belangrike bevinding is dat die vervoer beperkings in die poruese spoelbedekking en gasfase weglaatbaar klein is soos uitgebeeld deur die Damköhler en Fourier getalle onderskeidelik. Die eksperimentele

mikrokanaal reaktor het 'n 98.2% omskakeling van NH_3 en 'n drywingsdigtheid van $30.8 \text{ kW}_e \text{ L}^{-1}$ tydens toetse by die optimum bedryfs toestande wat daargestel is deur die model. Goeie ooreenstemming met eksperimentele data is bevind, so die geïntegreerde eksperimentele modelering benadering wat hier gebruik is kan 'n daadwerklike stap tot die effektiewe ontwerp van 'n ammoniak gedryfde mikrokanaalhervormer wees.

In Hoofstuk 5 is die vooruitsig om H_2 via ammoniak (NH_3) ontbinding te produseer evalueer in 'n alleenstaande eksperimentele mikrokanaal reaktor spoelbedek met 'n kommersiële Cs bevorderde $\text{Ru}/\text{Al}_2\text{O}_3$ katalisator (ACTA Hypermec 10010). Die reaktor uitset is ondersoek onder atmosferiese druk as funksie van reaksie temperatuur (723 – 873 K) en gas uurlikse ruimte snelheid ($65.2 - 326.1 \text{ NI g}_{\text{cat}}^{-1} \text{ h}^{-1}$). Ammoniak omskakeling van 99.8% is gedemonsteer by $326.1 \text{ NI g}_{\text{cat}}^{-1} \text{ h}^{-1}$ en 873 K. Die H_2 vervaardig by hierdie bedryfstoeestande was genoegsaam om 'n brandstofsels drywingsuitset van 60 W_e en 'n drywingsdigtheid van $164 \text{ kW}_e \text{ L}^{-1}$. Oor die algemeen het die Ru gebaseerde mikrokanaal reaktor die ander NH_3 mikrogestruktureerde hervormers uitgestof wat in die literatuur genoem is insluitend die Ni gebaseerde stelsel in Hoofstuk 3. Verder het die mikrokanaal reaktor 'n beter werksverrigting getoon teenoor 'n vastebedbuis mikroreaktor met dieselfde Ru gebaseerde katalisator. Die hoë H_2 deurset wat vertoon is mag die wydverspreide benutting van die Ru-gebaseerde mikroreaksie stelsel in hoë-drywing toepassings bevorder.

Vier gelyke hersiende joernaal publikasies en ses konferensie publikasies het die lig gesien as gevolg van hierdie werk.

Slutelwoorde: Ammoniak ontbinding, mikrokanaal reaktor, waterstof generasie, PEM brandstof sel, Uitset beoordeling, modelerings evaluasie

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LIST OF JOURNAL PUBLICATIONS RELATED TO THIS STUDY

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Chiuta S, Everson RC, Neomagus HWJP, van der Gryp P, Bessarabov DG. *Reactor technology options for distributed hydrogen generation via ammonia decomposition: A review. International Journal of Hydrogen Energy* 2013;38(35):14968–14991.

Chiuta S, Everson RC, Neomagus HWJP, Bessarabov DG. *Experimental performance evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation. International Journal of Hydrogen Energy* 2014;39(14):7225–7235.

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Chiuta S, Everson RC, Neomagus HWJP, Bessarabov DG. *Performance evaluation of a high-throughput microchannel reactor for ammonia decomposition over a commercial Ru-based catalyst. International Journal of Hydrogen Energy* 2015;40(7):2921–2926.

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Steven Chiuta, Ray Everson, Hein Neomagus, Dmitri Bessarabov. *Experimental investigation of an ammonia-fuelled microchannel reformer for hydrogen generation*. **24th Annual Conference of the Catalysis Society of South Africa.**, November 15-19 (2013), Wild Coast Sun, Port Edward, South Africa.

Steven Chiuta, Ray Everson, Hein Neomagus, Percy van der Gryp, Dmitri Bessarabov. *A CFD simulation of an ammonia-fuelled microchannel processor for hydrogen generation*. **23rd Annual Conference of the Catalysis Society of South Africa.**, November 11-14 (2012), Langebaan, South Africa.

Steven Chiuta, Ray Everson, Hein Neomagus, Dmitri Bessarabov. *The generation of hydrogen for PEM fuel cell applications via ammonia decomposition over Ni-PGM catalyst on mixed-oxide support*. **19th World Hydrogen Energy Conference.**, June 3-7 (2012), Sheraton Centre, Toronto, Canada.

Steven Chiuta, Dmitri Bessarabov. *Preliminary analysis of ammonia-based hydrogen generation strategies for fuel cell applications: thermo-catalytic decomposition and electrolysis*. **22nd Annual Conference of the Catalysis Society of South Africa.**, November 13-16 (2011), Muldersdrift, Johannesburg, South Africa.

Vasilica Lates, Steven Chiuta, Cobus Kriek, Dmitri Bessarabov. *Fundamentals and applications of ammonia and sulphur-dioxide electrolysis for hydrogen production*. **22nd Annual Conference**

of the Catalysis Society of South Africa., November 13-16 (2011), Muldersdrift,
Johannesburg, South Africa.

CHAPTER 1: INTRODUCTION

1.1 Overview

This work was motivated by the need for a convenient and efficient method of providing hydrogen for a proton-exchange membrane fuel-cell (PEMFC) intended for operation in portable and distributed power applications. As both portable and distributed hydrogen generators require small and lightweight systems, ammonia-fuelled microchannel reactors will play a key role in the development of appropriate fuel processing units. Although the production of hydrogen by ammonia decomposition has been used successfully at the industrial scale (such as in steel nitriding processes), hydrogen generation at the microscale presents reaction engineering challenges quite different to those encountered in industrial reactor design and development. The general objective of this work was, therefore, to undertake an experimental study of the ammonia-fuelled microchannel reformer and to use the reactor performance data to develop and validate a mathematical model which can be used in the development of effective and innovative designs for ammonia-fuelled microchannel reactors for PEM fuel cell power systems.

1.2 Background and problem statement

Fuel cells are widely regarded as an enabling technology towards a sustainable hydrogen (H_2) economy. Fuel cells directly convert chemical energy into electrical energy and with much higher efficiencies in comparison to internal combustion engines (Maltosz and Commenge., 2002). Various types of fuel cells such as proton exchange membrane fuel cells (PEMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), solid oxide fuel cells (SOFC), and direct methanol fuel cells (DMFC) are actively being researched worldwide for transportation, portable and distributed power applications. PEM fuel cells however continue to attract the most attention owing to their exceptional operational characteristics such as high power densities, quiet operation, and inherent ability to operate on near-zero pollution levels

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(Palo et al., 2002, Holladay et al., 2004, Son et al., 2008). Hydrogen is the preferred feed to the PEM fuel cell since it has the highest gravimetric energy density (120 MJ kg^{-1}) of any common fuel and its combustion product (water) is environmentally-harmless.

In spite of the growing interest, the breakthrough of fuel cell technology at a large scale is still far from accomplishment. The principal obstacle remains the lack of a sustainable (easy, safe, and cheap) infrastructure to deliver H_2 fuel to the PEM fuel cell. Whereas H_2 is the best fuel from a performance standpoint, it is not found in nature in appreciable quantities, and it is not a fuel that is easy to carry around for portable and distributed applications. In fact, the extremely low volumetric energy density of H_2 aggravates its storage and transportation difficulties. Although many different ways exist to store H_2 , none of them have proven effective at storing H_2 at high energy densities.

For example, compressed gas storage offers only a near-term option for early markets, but the cost of lightweight composite tanks is still a daunting challenge (Stetson, 2013). Likewise, H_2 liquefaction requires a large amount of energy and suffers from boil-off losses during storage (Sherif et al., 1997, Ahluwalia and Peng, 2008). In the interim, material-based storage using metal hydrides is promising, but slow H_2 desorption kinetics and the large weight of the hydride materials are the main problems (McWhorter et al., 2011, Stetson, 2013). Consequently, there exists a wide gap in the H_2 supply chain portrayed by the present lack of an adequate infrastructure for generating and delivering H_2 to drive PEM fuel cell systems. For this reason, fuel processing for on-demand hydrogen generation from an easily stored liquid fuel such as ammonia is actively investigated in this thesis. As both portable power generation and distributed energy systems require compact systems, microreactor technology will play a key role in the development of an ammonia fuel processor for the in-situ generation of clean hydrogen. The design challenges and limitations for ammonia-fuelled microchannel reactors in particular, are elucidated in Appendix B.3.3.

1.3. Thesis motivation and rationale

The on-demand generation of H₂ fuel via chemical or thermal processing of liquid H₂ carriers is a promising solution at least until problems of H₂ storage and economics are sufficiently resolved (Holladay et al., 2004, Ahluwalia et al., 2005). Table 1-1 shows some of the common liquid H₂ carriers as well as their gravimetric and volumetric densities. These H₂ carriers are easier to transport and storage conditions are much less severe compared to compressed gas and liquefaction systems. Among the various H₂ carriers (see Appendix B.4), ammonia (NH₃) has been continuously suggested and its subsequent processing (NH₃ decomposition, also known as NH₃ reforming) is gaining considerable interest for PEM fuel cell applications (Choudhary et al., 2001, Yin et al., 2004, Lan et al., 2012, Chiuta et al., 2013). This emergence is partly due to the fact that NH₃ is a carbon-free H₂ carrier that has superior H₂ content and gravimetric energy density (Table 1-1). A base case for NH₃ decomposition was exhaustively explicated in Chiuta et al. (2013), which also happens to be Chapter 2 of this thesis and therefore will not be repeated here.

Table 1-1 Gravimetric and volumetric energy densities of common liquid H₂ carriers

Fuel	H ₂ content (wt %)	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/L)
Ammonia	17.7	4 318	4 325
Methanol	12.5	6 400	4 600
Methanol (incl. water*)	-	2 040	-
Ethanol	13	7 850	6 100
Ethanol (incl. water*)	-	2 578	-
Gasoline	15.8	12 200	9 700
Gasoline (incl. water*)	-	2 140	-

* Including mass of water for steam reforming - hydrocarbons require water for steam reforming to produce hydrogen, and this reduces their initially high energy densities.

Ammonia decomposition has been studied a long time but only for gaining more fundamental knowledge on kinetics of NH₃ synthesis (Yin et al., 2004). The interest towards distributed H₂ production for PEM fuel cell applications is only recent, and research has concentrated more on catalyst development. The potential value of H₂ generation via NH₃

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decomposition is however reduced unless due consideration is given to the development of necessary reactors. In Fig. 1-1 (left), summative statistics of 10 years research on developments in reactor infrastructure for NH_3 decomposition are shown. An average publication rate of 3 papers per year is obviously inadequate and much remains to be done to advance NH_3 decomposition as a fuel processing technology for distributed H_2 generation.

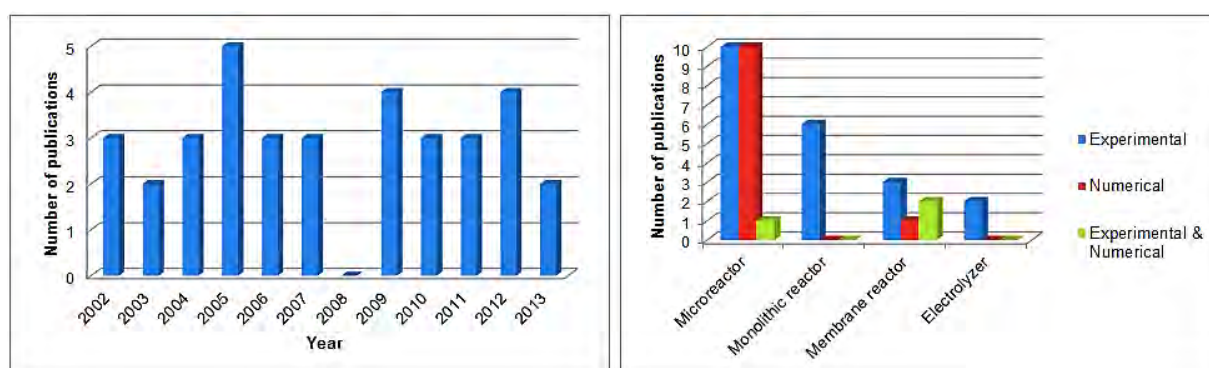


Fig. 1-1 Number of publications per year since 2002 for NH_3 decomposition reactor infrastructure (left). Distribution of publications on NH_3 decomposition reactor infrastructure by study design (right). Reprinted from Chiuta et al. (2013), Copyright 2013, with permission from Elsevier.

Ammonia decomposition has also been used successfully for nitriding in the steel industry (Djega-Mariadassou et al., 1999). Nitriding requires partial NH_3 decomposition and conventional fixed-bed reactors are used. On the contrary, a clean H_2 supply is required for PEM fuel cell applications. This presents reaction engineering problems that are distinct from those in conventional fixed-bed reactors (also see Appendix B.3.2). Specifically, large temperature gradients exist within these large reactors and the extent of the endothermic NH_3 decomposition reaction is reduced. In addition, fixed-bed reactors far exceed the critical requirements (compactness, low weight, and rapid transient response) for distributed H_2 systems as specified in the USDOE 2015 (Satyapal et al., 2007).

Conversely, innovative reactor technologies present a platform to advance NH_3 decomposition for PEM fuel cell applications. Fig. 1-1 (right) reveals that microreactors are at a relatively more advanced research and development phase than any of the other reactor

technologies. These reactors have the potential to satisfy all critical requirements for portable and distributed H_2 generation via NH_3 decomposition. Most importantly, microchannel reactors enable on the one hand to reduce substantially the size footprint of the overall system and on the other hand enhance the heat and mass transfer rates (50 to 100 times) by virtue of their small channels which give rise to small diffusion paths (Lerou et al., 1996, Jensen, 2001, Worz et al., 2001, Kolb and Hessel, 2004).

Very little work is however reported in literature on experimental investigation of microchannel reactors for NH_3 decomposition. Likewise, mathematical (numerical) modelling has not been explored enough to establish design standards for ammonia-fuelled microchannel reactors. Worse still, the well-founded design rules for macroscale reactors do not translate directly to the microscale. An integrated experimental and mathematical approach can help attain accurate designs and optimal operational philosophies for the microscale. Yet, Fig. 1-1 (right) reveals the use of this important approach towards ammonia-fuelled microchannel reactors is practically nonexistent. The general objective of this work was therefore to undertake an experimental and mathematical modelling evaluation of a microchannel reactor for NH_3 decomposition.

1.4. HySA Infrastructure: A national hydrogen program initiative for South Africa

The work described in this thesis was part of a larger national project branded Hydrogen South Africa (HySA) and funded by the government of South Africa through the Department of Science and Technology (DST). HySA was launched as a government initiative to create high-value research and development capability within hydrogen and fuel cell technologies whilst adding value to the local platinum group mineral (PGM) resources (Bessarabov et al., 2012). Incidentally, South Africa has 75% of the world's PGM reserves, hence hydrogen and fuel cell technologies present an opportune market for value-addition of these reserves owing to the

inherent demand for PGM-based catalysts. The HySA program consists of three Centres of Competence namely HySA Infrastructure, HySA Catalysis, and HySA Systems. This work was done under the auspices of the HySA Infrastructure Centre of Competence, which is co-hosted by North-West University (Potchefstroom Campus) and the Council for Scientific and Industrial Research (CSIR, Pretoria). The HySA Infrastructure project framework (Fig. 1-2) consists primarily of three programs, namely; Electrolyzer and electrolyzer systems, H_2 storage and production, and Biological H_2 production. This thesis was done under the theme of “chemical H_2 production” within the H_2 storage and production program.

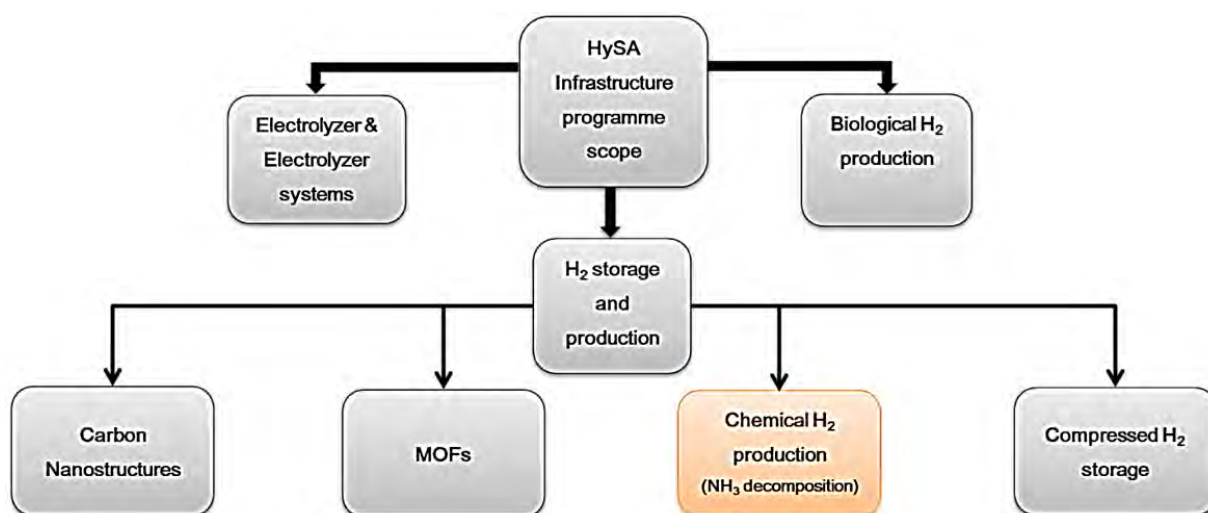


Fig. 1-2 HySA Infrastructure programme framework

1.5 Research Aims and Objectives

This thesis presents an integrated experimental-mathematical modelling approach towards achieving accurate designs and operating conditions for ammonia-fuelled microchannel reactors. Therefore, the general objectives of this thesis are two-fold: (1) to experimentally evaluate the operation and performance of the microchannel reactor and, (2) to provide a mathematical framework for analyzing and understanding the physical and chemical origins of observed microchannel reactor performance. The specific objectives of the study are:

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- I. To review the state-of-the-art in innovative reactor technologies for distributed H_2 production via pure NH_3 decomposition. Which reactor technology is most promising to advance NH_3 decomposition for fuel cell applications? What are the existing technology gaps to contend with in implementing this reactor technology?
- II. To evaluate, characterize, and demonstrate miniaturized H_2 production in a Ni-based ammonia-fuelled microchannel reactor. What are the performance limits of the microchannel reactor relative to the residual NH_3 tolerance for PEM fuel cells?
- III. To develop a valid mathematical model suitable for obtaining fundamental insight into the operation and performance of the microchannel reactor. What is the importance of transport properties and reaction parameters on microchannel reactor performance? How does the reactor operation depend on these parameters? Can we make design changes to improve the operational performance?
- IV. To evaluate the performance of a Ru-based ammonia-fuelled microchannel reactor. How does this performance compare with that attained in the Ni-based microchannel reactor?

1.6. Research Design and Methodology

The research approach used in this thesis integrated experimental and mathematical modelling techniques to evaluate an ammonia-fuelled microchannel reactor operating to generate H_2 for fuel cell applications. The Ni-based microchannel reactor performance was first assessed in a series of experiments where operating conditions were varied accordingly. Next, CFD modelling was used to simulate reactive flow and analyze the velocity, temperature, concentration, and reaction rate profiles within the Ni-based microchannel reactor. The model consisted of mass, energy and momentum balance equations and solutions were obtained via a Finite Element Method (FEM) where the solution algorithm was completed using the COMSOL

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Multiphysics™ software (Comsol, Inc., version 4.3a). Most importantly, the model was validated using the obtained experimental data. In addition, an experimental performance evaluation of a Ru-based microchannel reactor having identical geometry was done and fair comparisons between the two reaction systems were made. A CFD modelling evaluation of the Ru-catalyzed microchannel reactor was not undertaken as a consequence of the lack of reliable (experimentally-determined) kinetic rate law for pure NH_3 decomposition on the Ru-based catalyst. In order to obtain meaningful (non-speculative) analysis of the different transport phenomenon and dynamics occurring within the microchannel reactor, the chemical reaction kinetics must be available. The evaluation of NH_3 decomposition kinetics over the Ru catalyst is outside the scope of the present study, and is recommended for future work.

1.7 Outline of thesis

This thesis is presented in six chapters that include four original peer-reviewed articles (already published). Each chapter is written as a peer-reviewed article and can therefore be read independent of the entire thesis. Inevitably, some information is repeated throughout the thesis chapters, particularly in the introduction sections. The chapters are presented in the original form of the published articles and no changes have been made thereof. Following this introductory chapter;

- **Chapter two:** Presents a review article [published in the International Journal of Hydrogen Energy 2013;38(35):14968–14991], which provides an extensive review of the state-of-the-art reactor technology for pure NH_3 decomposition.
- **Chapter three:** Presents an original full-length article [published in the International Journal of Hydrogen Energy 2014;39(14):7225–7235], which describes the evaluation of the Ni-based microchannel reactor performance. The effects of reactor temperature and space velocity on key performance parameters are investigated.

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- **Chapter four:** Presents an original full-length article [published in the International Journal of Hydrogen Energy 2014;39(22):11390–11402], in which an ammonia-fuelled microchannel reactor is simulated in a three-dimensional (3D) CFD model that provides an understanding of reaction-coupled transport phenomena within the microchannel reactor.
- **Chapter five:** Presents a short communication (research note) [submitted to the International Journal of Hydrogen Energy 2014], which describes the evaluation of NH_3 decomposition in an experimental stand-alone Ru-based microchannel reactor. The obtained performance is compared with the Ni-based microchannel reactor as well as other microstructured reactors considered in literature.
- **Chapter six:** Contributions of this thesis and suggestions for the future work are summarized

References are provided at the end of each chapter. The references used in Chapter one and Appendix B (supplementary literature) are listed according to the requirement stipulated in the manual for post-graduate studies of the North-West University. The references used in Chapters two, three, four, and five are provided as specified by the journal in which the articles were published.

1.8 Authorship

Steven Chiuta was involved in all aspects of this thesis including the study design, laboratory experiments design and implementation, CFD simulations, data analysis and manuscript writing (lead author) of the four articles that make up this Ph.D thesis.

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CHAPTER 2: REACTOR TECHNOLOGY OPTIONS FOR DISTRIBUTED HYDROGEN GENERATION VIA AMMONIA DECOMPOSITION: A REVIEW

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Abstract

Hydrogen (H₂) fuel obtained via thermo-catalytic ammonia (NH₃) decomposition is rapidly attracting considerable interest for portable and distributed power generation systems. Consequently, a variety of reactor technologies are being developed in view of the current lack of infrastructure to generate H₂ for proton exchange membrane (PEM) fuel cells. This paper provides an extensive review of the state-of-the-art reactor technology (also referred to as reactor infrastructure) for pure NH₃ decomposition. The review strategy is to survey the open literature and present reactor technology developments in a chronological order. The primary objective of this paper is to provide a condensed viewpoint and basis for future advances in reactor technology for generating H₂ via NH₃ decomposition. Also, this review highlights the prominent issues and prevailing challenges that are yet to be overcome for possible market entry and subsequent commercialization of various reactor technologies. To our knowledge, this work presents for the first time a review of reactor infrastructure for distributed H₂ generation via NH₃ decomposition. Despite commendable research and development progress, substantial effort is still required if commercialization of NH₃ decomposition reactor infrastructure is to be realized.

Keywords: reactor infrastructure, ammonia decomposition, distributed hydrogen generation, PEM fuel cell

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2.1. Introduction

The world today faces critical challenges defined by gradually depleting non-renewable fossil fuel reserves and the likelihood of global warming in the wake of a rapidly growing global population. These simultaneous challenges threaten an energy and environmental crisis that is expected to have far-reaching socio-economic consequences. The predicament is further aggravated by the dynamic economic expansion associated with many developing countries, which places great demands on existing power and energy resources. One of the common responses of national governments in developing nations has been to implement power-rationing strategies widely known as “load-shedding”. As a result, essential service providers such as hospitals, banks, and telecommunication networks have resolved to reduce the adverse socio-economic impacts of load-shedding by using large battery banks and diesel generators as back-up power sources. In most cases, these back-up power devices often become prime power sources as power outages may last longer than anticipated. Unfortunately, conventional back-up power sources have several disadvantages, which will be elucidated below.

Diesel generators, for example, emit environmentally harmful greenhouse gases and operate at high noise levels. The latter is undesirable particularly where a quiet setting such as an office environment is considered essential. Battery power and run time have appreciably reduced in view of increased sophistication and functionalities of modern electronic devices [1]. In addition, diesel generators and battery banks have reportedly been vandalised at isolated telecommunication base stations and valuable items such as diesel fuel and important battery components have become targets for theft. Clearly, the extensive effects of the energy crisis are widely acknowledged and there is general agreement about the need to find alternative, sustainable power sources for a wide variety of applications. An attractive business case for distributed hydrogen generation in developing economies is power supply at off-grid (isolated) telecommunication towers. Approximately 640,000 off-grid cell-phone towers are powered by

diesel generators worldwide, while new off-grid installations are growing at 12% per annum [2]. We appreciate the importance of a diverse future energy mix, and distributed H₂ generation will be crucial in meeting our future energy needs. Table 2-1 shows the energy densities of common fuels that may be used to generate H₂ in distributed power systems. Note in particular that Table 2-1 also reveals the low energy density of current battery technology in relation to common fuels.

Table 2-1 Specific and volumetric energy densities of common fuels and power sources [3, 4]

Fuel	H ₂ content (wt %)	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/L)
Ammonia	17.7	4 318	4 325
Methanol	12.5	6 400	4 600
Methanol (incl. water*)	-	2 040	-
Ethanol	13	7 850	6 100
Ethanol (incl. water*)	-	2 578	-
Hydrogen (700 bar)	100	39 000	1 305
Gasoline	15.8	12 200	9 700
Gasoline (incl. water*)	-	2 140	-
Li-polymer battery	-	110	300

* Including mass of water for steam reforming

Proton exchange membrane (PEM) fuel cells have received great consideration as alternative power sources (see Appendix B) that demonstrate momentous potential to offset the adverse consequences of the global energy and environmental crisis [5,6]. The attractiveness of PEM fuel cells derives from exceptional operational characteristics such as high power densities, quiet operation, and inherent ability to generate zero pollution. In addition, PEM fuel cells have higher efficiencies than combustion-based power sources because the Carnot factor does not affect energy conversion in fuel cells [7]. Despite being a mature technology having these superior attributes, several obstacles continue to hinder the widespread adoption of PEM fuel cells for distributed power generation systems. Principally, the volumetric energy density of hydrogen (preferred fuel for PEM fuel cells) is low so as to render its storage and transportation difficult. In fact, H₂ has the lowest volumetric energy density of any fuel. Consequently, there

exists a wide gap in the H_2 supply chain illustrated by the present lack of an adequate infrastructure for generating and delivering H_2 to drive PEM fuel cell systems.

The on-site generation of H_2 in fuel processors is considered a promising stop-gap solution at least until problems of hydrogen storage and economics are sufficiently resolved [5,8]. Regrettably, there are no known ready sources of H_2 on earth but different H_2 -containing compounds having adequate energy densities are available for fuel processing to liberate H_2 (Table 2-1). However, early market penetration of fuel processing technologies is hugely dependent on the cost of fuel processor hence the fuel choice is considered a major factor [9]. In view of this, the use of ammonia (NH_3) as a carbon-free H_2 carrier has been suggested repeatably. In fact, NH_3 decomposition is one of the fuel processing technologies gaining considerable interest for PEM fuel cell applications [10–15]. NH_3 decomposition has been studied a long time for numerous reasons, e.g. to gain more fundamental knowledge on the kinetics of NH_3 synthesis; the interest towards distributed H_2 production is only recent.

There are several technical and economic reasons in support of NH_3 decomposition for distributed H_2 generation. First and foremost, NH_3 decomposition has a single feed stream and is therefore accomplished in a single step. For this reason, there is a significant cost advantage in consequence of reduced balance-of-plant (BOP) as compared to the multi-step process (Fig. 2-1) inherent in steam reforming of hydrocarbons [16]. Also, there are no complex mass management challenges to deal with in NH_3 decomposition, such as feed ratio or selectivity issues which are prevalent in steam reforming of hydrocarbons. Table 2-1 shows that the gravimetric energy densities of hydrocarbon fuels are effectively reduced when the weight of water for steam reforming is included, so that NH_3 becomes especially competitive with respect to specific energy. Moreover, NH_3 is an inexpensive fuel (US\$₂₀₁₂530/ ton) that has an extensive and well-developed manufacturing-distribution infrastructure worldwide to guarantee uninterrupted fuel supply. Actually, the large investment otherwise needed to develop a new

system for H_2 can be avoided owing to this well-established distribution network. Furthermore, the availability of NH_3 is incontestable given that the annual global NH_3 production capacity continues to grow by more than 20% [17]. In summary, NH_3 decomposition is particularly attractive as a fuel processing technology for PEM fuel cell applications from a cost, system volume, and logistics perspective.

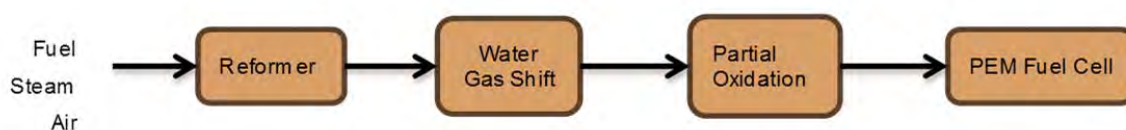


Fig. 2-1 Schematic of a fuel processing system based on hydrocarbon fuel.

However, there are perceptions and potential operational obstacles that could hinder the prospects for distributed H_2 generation via NH_3 decomposition. It is important these views be discussed to dispel associated uncertainties. Most importantly, PEM fuel cells have exceptionally low residual NH_3 tolerance (0.1 ppm NH_3) that may well present significant operational challenges. Specifically, residual NH_3 concentration above the specified limit has been observed to deactivate the anode catalyst and subsequently lead to loss in cell performance [18]. It is difficult for a stand-alone ammonia fuel processor to attain this stringent tolerance limit while maintaining economic operation as thermodynamics dictate extremely high temperature operation. However, small weights (<100 g) of commercially available adsorbents such as AmmoSorb™ have been shown to reduce residual NH_3 to 1 ppb levels [10,19–21]. The small adsorbent required potentially makes for easy integration into space-constrained (portable) devices. The potential lifetime of these sorbents for PEM fuel cell operation however have not been investigated

Besides, emerging high-temperature PEM (HT-PEM) fuel cells have a greater potential to resist NH_3 poisoning than low-temperature PEM fuel cells [22]. However, no study has ever tested this hypothesis but if it proves true, then HT-PEM cells can subsequently be an enabling

gamechanger possibly improving the prospects for NH_3 decomposition as a fuel processing technology for distributed H_2 generation. Already, HT-PEM fuel cells have shown significant resistance against carbon monoxide (CO) poisoning and instances have been reported where these have operated on a fuel feed containing as much as 5% CO, which is 5 000 times more than the 10 ppm CO restriction applicable to low-temperature fuel cells [23]. Alternatively, alkaline PEM fuel cells (AFC) can effectively operate directly on H_2 fuel generated from NH_3 decomposition without any need for NH_3 clean-up [12,24]. With all these possible measures in place, the severe threat posed by residual NH_3 to the implementation of NH_3 decomposition for PEM fuel cell applications can be significantly reduced.

At this point, we refer the reader to a position paper in which the US Department of Energy (USDOE) specifically rejects NH_3 for onboard storage in their national program [25]. Their decision was based solely on the inability of then existing NH_3 decomposition fixed-bed reactors to satisfy prescribed system performance criteria such as weight, volume, and start-up time. We concede that reducing the size and weight of a H_2 production system is a necessary requirement for onsite and onboard applications. In fact, it is one of the engineering-oriented targets specified by the USDOE and the US Council for Automotive Research [26]. However, onboard H_2 generation via NH_3 decomposition was successfully demonstrated in the Silver Volt electric car project following collaboration between the Technical University of Graz and Apollo Energy Systems [12]. In this paper, we endeavour to demonstrate how recent advances in NH_3 decomposition reactor infrastructure can help diffuse some of the perceived inadequacies and certainly warrant reconsideration of “ammonia for hydrogen” in national hydrogen energy programs and technology roadmaps.

We acknowledge the negative views concerning the toxicity of NH_3 , but note also significant studies that support its acceptable use as a fuel. MesoSystems Inc. and Intelligent Energy Inc. developed and patented an intrinsically safe fuel-storage system for ammonia and propane that

significantly downplays the “toxicity card” [27,28]. Upon bullet puncture, their lightweight 0.8 L titanium fuel storage tank was able to control the NH_3 release that its concentration in the immediate environment remained below the 300 ppm immediately dangerous to life and health (IDLH) limit. In another relevant study, Duijm et al. [29] assessed NH_3 as a transportation fuel and concluded its safety to be comparable to that of gasoline, which can be considered safe. Also, Quest Consultants Inc. [30] performed a comparative quantitative risk assessment in which they demonstrated and confirmed the safety of NH_3 fuel in transportation applications. More so, the small fuel storage capacity in portable devices means there is a low probability of exceeding the IDLH exposure limit in case of a leak. Notwithstanding, we are not aware of any other significant safety, technical or economic barriers that could hinder the attractiveness of an ammonia-mediated hydrogen economy.

The development of NH_3 decomposition infrastructure for distributed power generation via PEM fuel cells has focused mainly on catalyst development, which has been extensively covered elsewhere [10,11]. Ruthenium (Ru) is considered the best catalyst for NH_3 decomposition but is too expensive to be widely used and has a short catalytic lifetime [31]. Conversely, nickel (Ni) gives the best performance among the cheap metals and is therefore widely accepted as a viable alternative to Ru [10]. However, the potential value of H_2 generation via NH_3 decomposition is reduced unless consideration is given to development of the necessary reactor infrastructure. This paper provides an overview of past and recent developments in reactor infrastructure for distributed H_2 production via NH_3 decomposition. Further, we highlight the position of NH_3 decomposition as an ideal energy vector in a future energy mix.

2.2. Thermodynamic considerations

To give perspective to the discussions that follow, a brief summary of NH₃ decomposition thermodynamics is necessary. To begin with, NH₃ decomposition occurs according to the following chemical equation;



NH₃ decomposition is a mildly endothermic reaction, whose conversion depends on temperature. It is also equilibrium-limited and therefore requires relatively high temperatures to achieve sufficiently high single-pass conversions [11]. To provide an idea of the maximum theoretically obtainable conversions, thermodynamic equilibrium calculations were performed for a temperature range of 250–700 °C (Table 2-2). The values of equilibrium conversions of NH₃ to H₂ under these different temperature conditions were calculated using HSC Chemistry 7 software via the Gibbs free energy minimization method.

Table 2-2 Equilibrium NH₃ conversion (at 1 bar pressure) as a function of reaction temperature

Temperature (°C)	250	300	350	400	450	500	600	700
NH ₃ conversion (%)	89.20	95.70	98.10	99.10	99.50	99.70	99.90	99.95

Table 2-2 shows that temperatures above 400 °C are needed to reach virtually complete NH₃ decomposition (>99%). In addition, thermodynamic calculations show that equilibrium limitations are negligible and the reaction is essentially irreversible at temperatures above 450 °C. Also, the conversion becomes less dependent on temperature above 450 °C so that results may be interpreted in terms of kinetic rather than thermodynamic limitations.

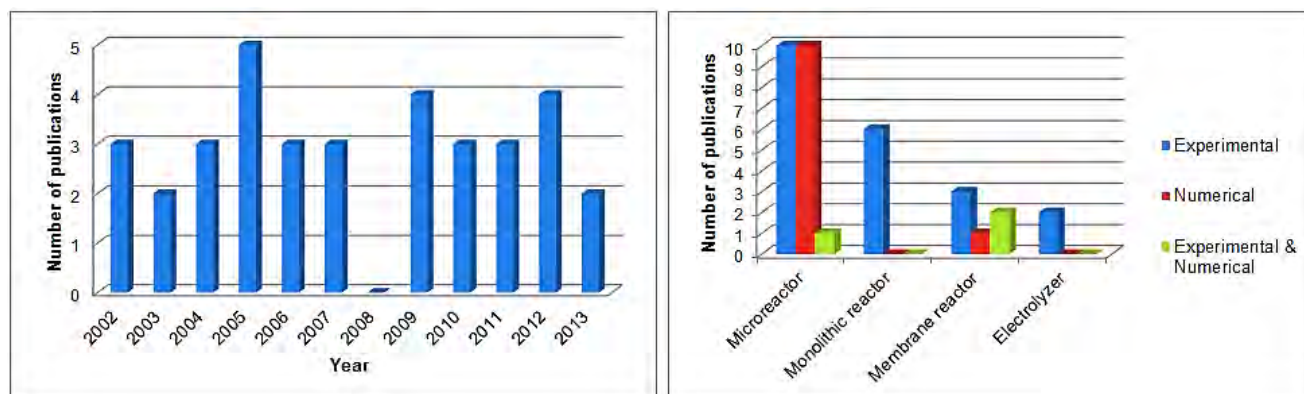


Fig. 2-2 Number of publications per year since 2002 for NH₃ decomposition reactor infrastructure (left). Distribution of publications on NH₃ decomposition reactor infrastructure by study design (right).

2.3. Reactor infrastructure for ammonia decomposition

This section reviews the various reactor technologies (infrastructure) that have been developed to generate H₂ for distributed PEM fuel cell application via NH₃ decomposition. Specifically, an overview is presented on the following NH₃ decomposition reactor infrastructure found in the open literature: microreactors, monolithic reactors, multifunctional membrane reactors, and electrochemical reactors vis-à-vis NH₃ electrolyzers. Table 2-3 and 2-4 present a summary of the literature according to first appearance, whilst Fig. 2-2 provides summative statistics of publications on developments in reactor infrastructure for distributed H₂ production via NH₃ decomposition.

Chapter 2: Reactor technology options for distributed hydrogen generation via ammonia decomposition: A review

Table 2-3 A summary of literature on experimental investigation of reactor infrastructure for NH₃ decomposition

Author	Year	Reactor type	Reactor dimensions	Study design	Reactor conditions	NH ₃ conversion
Powell et al. [24]	2002	Microchannel Reactor	L = 50 mm	Experimental	T = 600 °C P = 1 bar	>99.5%
Arana et al. [40]	2003	Suspended-tube microchannel reactor	L = 3 mm W = 500 µm H = 500 µm T _{walls} = 2 µm	Experimental and 2D heat transfer modelling	6 NmL/min NH ₃ T = 900 °C P = 1 bar	97.0%
Ganley et al. [41]	2004	Post microreactor	L = 2.1 cm H = 3 mm V = 0.3 cm ³	Experimental	15 NmL/min NH ₃ T = 650 °C P = 1 bar	85.0%
Ganley et al. [50]	2004	Microchannel reactor	L = 9.2 mm W = 140 µm V = 0.35 cm ³	Experimental	145 NmL/min NH ₃ T = 600 °C P = 1 bar	99.0%
Sorensen et al. [55]	2005	Microchannel reactor	L = 8 mm W = 200 µm H = 200 µm V = 20 µL	Experimental	T = 365–650 °C P = 1 bar	-
Vitse et al. [101]	2005	Electrolyzer	-	Experimental	T = 30 °C P = 1 bar	100.0%
Sorensen et al. [57]	2006	Microchannel reactor	L = 8 mm W = 1.5 mm H = 0.3 mm	Experimental	T < 227 °C P = 1 bar	-
Christian et al. [71]	2006	Interconnected pore monolithic reactor	V = 1.05 cm ³	Experimental	36 NmL/min NH ₃ T > 700 °C P = 1 bar	99.9%
Zhang et al. [88]	2006	Membrane reactor	-	Experimental	50–400 NmL/min NH ₃ T = 425–500 °C P = 1–5 bar	55–99%
Lu et al. [73]	2007	Microfibrinous monolithic reactor	V = 0.5 cm ³	Experimental	145 NmL/min NH ₃ T = 600 °C P = 1 bar	99.0%
Lu et al. [74]	2007	Microfibrinous monolithic reactor	V = 0.9 cm ³	Experimental	150 NmL/min NH ₃ T = 650 °C P = 1 bar	99.4%
Liu et al. [75]	2007	Microfibrinous monolithic reactor	V = 0.5 cm ³	Experimental	145 NmL/min NH ₃ T = 650 °C P = 1 bar	99.5%
Israni et al. [92]	2009	Membrane reactor	-	Experiments and 1D heterogeneous model	30–700 NmL/min NH ₃ T = 500–600 °C P = 3–5 bar	60–100%
Wang et al. [10]	2009	Microfibrinous monolithic reactor	V = 50 cm ³	Experimental	1100 NmL/min NH ₃ T = 600 °C P = 1 bar	>99.9%
Boggs and Botte [100]	2009	Electrolyzer	-	Experimental	T = 30 °C P = 1 bar	100.0%
Plana et al. [76]	2010	Honeycomb monolithic reactor	L = 65 mm D = 10 mm	Experimental	100 NmL/min NH ₃ T = 600 °C P = 1 bar	>99.0%
Li et al. [94]	2011	Catalytic membrane reactor	L = 10 cm D = 10 mm	Experimental	10 NmL/min NH ₃ T = 450 °C P = 1 bar	45.0%
Kim and Kwon [62]	2011	Integrated microreactor	L = 55 mm D = 16 mm	Experimental	10 NmL/min NH ₃ P = 1 bar Efficiency = 13.7%	98.0%
Kim et al. [65]	2012	Integrated microreactor	L = 55 mm D = 16 mm	Experimental	10 NmL/min NH ₃ P = 1 bar Efficiency = 10.4%	97.0%
Li et al. [96]	2012	Catalytic membrane reactor	L = 10 cm D = 10 mm	Experimental	40 NmL/min NH ₃ T = 450 °C P = 1–3 bar	74.4%
Li et al. [97]	2013	Catalytic membrane reactor	L = 10 cm D = 10 mm	Experiments and 1D mathematical modelling	0.02–0.13 mol/h NH ₃ T = 390–470 °C P = 1 bar	45–95%

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Table 2-4 A summary of literature on numerical investigation of reactor infrastructure for NH₃ decomposition

Author	Year	Reactor type	Reactor dimensions	Study design	Reactor conditions	NH ₃ conversion
Deshmuck et al. [49]	2004	Post microreactor	L = 2.1 cm H = 3 mm V = 0.3 cm ³	1D PFR microkinetic model and 2D CFD modelling	5–145 NmL/min T = 650 °C P = 1 bar	35–95%
Deshmuck and Vlachos [38]	2005	Spatially coupled microchannel reactor (countercurrent)	L = 1 cm W = 300 μm H = 150 μm T _{walls} = 300 μm	2D CFD modelling	U _{inlet} = 0.05–0.35 m/s T > 900 °C P = 1 bar	>99.0%
Deshmuck and Vlachos [53]	2005	Spatially coupled microchannel reactor (cocurrent)	L = 1 cm W = 300 μm H = 150 μm T _{walls} = 300 μm	2D CFD modelling	U _{inlet} = 0.05–0.35 m/s T > 900 °C P = 1 bar	>99.0%
Waghode et al. [54]	2005	Microchannel reactor	L = 1.5 cm W = 0.5 cm	2D flow and heat transfer modelling	U _{inlet} = 0.01 m/s T = 600 °C P = 1 bar	88.7%
Kaisare et al. [58]	2009	Spatially coupled microchannel reactor	L = 5 cm W = 200 μm T _{walls} = 750 μm	1D heterogeneous CFD modelling	U _{inlet} = 0.92–5 m/s T = 800–1500 °C P = 1 bar	99.0%
Chein et al. [59]	2010	Packed-bed microreactor	L = 20 mm D = 10 mm	1D steady-state model	0.025 mol/h T = 600 °C P = 1–2 bar	>99.0%
Alagharu et al. [18]	2010	Packed-bed microreactor	L = 31 cm D = 5 mm	1D mathematical modelling	0.9 mmol/s T > 527 °C P = 2 bar	>99.5%
Di Carlo et al. [11]	2011	Membrane reactor	V = 30 cm ³	3D CFD modelling	U _{inlet} = 1–2 cm/s	99.9%
Chen et al. [47]	2012	Post microreactor	L = 14 mm H = 5 mm	LBM numerical modelling	< 50 NmL/min T > 627 °C P = 1 bar	>95.0%
Chiuta et al. [67]	2012	Microchannel reactor	L = 5 cm W = 450 μm H = 150 μm T _{walls} = 250 μm	3D CFD modelling	< 50 NmL/min T = 450–700 °C P = 1 bar	4–99.9%
Regatte and Kaisare [68]	2013	Spatially coupled microchannel reactor (crossflow)	L = 10 mm H = 300 μm	2D CFD modelling	14 NmL/min T > 1000 °C P = 1 bar	>99.0%

2.3.1 Microreactor infrastructure for ammonia decomposition

Microreaction technology (MRT) is a relatively new field that began in the early 1990s. MRT was adapted from micro-electro-mechanical systems (MEMS) technology which uses ultra-compact microchannel heat exchangers to cool electronic packages that operate at high heat fluxes [32–34]. MRT consists of reactors that have characteristic lengths in the sub-millimeter range. The small length scale greatly increases the surface-to-volume ratio and several consequential advantages arise which include, but are not limited to, enhanced heat and mass transfer rates [35–37]. In particular, heat transfer coefficients in microreactors have been

reported to be 50–100 times greater than those for conventional fixed-bed reactors [38]. Consequently, numerous organizations today are active in the fabrication and exploration of MRT-based systems. To name a few, organizations such as Institut für Mikrotechnik Mainz (IMM), Velocys Inc., and Institute of Micro Process Engineering (IMVT) at Karlsruhe Institute of Technology (formerly Forschungszentrum Karlsruhe) have been leading in the field of MRT.

The critical requirements for distributed power systems as specified in the USDOE 2015 targets include compactness, low weight, and rapid response [25]. The conventional fixed-bed reactors inherently have size and weight characteristics that far exceed specified requirements. The implication is that large temperature gradients exist within the reactor and the extent of the endothermic NH_3 decomposition reaction is reduced. However, microreactor technology can eliminate temperature gradients (cold or hot spots) owing to high heat transfer coefficients made possible by small diffusion paths. The general stance of associating high operating temperatures with large reactors is irrelevant in the context of MRT. In view of these attributes, microreactors provide a feasible reactor infrastructure that certainly warrants consideration for portable and stationary H_2 generation for PEM fuel cell applications.

The use of microreactors is nonetheless beneficial to certain class of reactions, namely, fast catalytic reactions which consume or generate large reaction heat [35,39]. The appropriateness of microreactors for fast reactions is due to the small channel size, which dictates short residence times in the order of milliseconds. The fast kinetics of the ammonia decomposition reaction has been demonstrated elsewhere and residence times in the order of milliseconds have been reported [20,40,41]. With regard to reaction heat, the endothermic NH_3 decomposition occurs at high temperatures to attain high conversion with fast kinetics, indicating strong heat transfer limitations. In a microreactor, heat transfer resistance is minimised and the overall reactor performance is dictated by intrinsic chemical kinetics rather

than by heat or mass transfer. MRT is therefore a suitable candidate technology for investigating NH_3 decomposition.

MesoSystems Technology Inc. and Intelligent Energy Inc. developed a compact, NH_3 -based H_2 generator rated at 50 W power supply [27,28,42,43]. Their system comprised of lightweight MesoChannel™ ammonia cracking reactor, high-effectiveness heat exchangers, high-capacity NH_3 adsorbent, and flow/temperature control components [43]. NH_3 was decomposed on an unspecified catalyst at approximately 600 °C to generate a product mixture of H_2 and N_2 with residual NH_3 concentrations in the range 0.2–0.5 wt% [28]. The residual NH_3 was removed using a proprietary carbon adsorbent with a capacity to adsorb 10 wt% NH_3 [19]. However, the adsorbent lifetime or longevity was not reported and the question of adsorbent overload still remains sufficiently critical to warrant experimental investigation. The NH_3 -free product gas was fed to a PEM fuel cell to generate power for portable military devices. The system targets included a 5 min start-up time and 1000 Wh electric power in a one-litre (1 kg) package. Their microreactor was integrated to an HPower Corporation SSG-50 fuel cell, but the performance and system stability data are not reported in open literature. Thermal management for the reactor system was accomplished using compact heat exchangers and innovative high-temperature vacuum insulation panels.

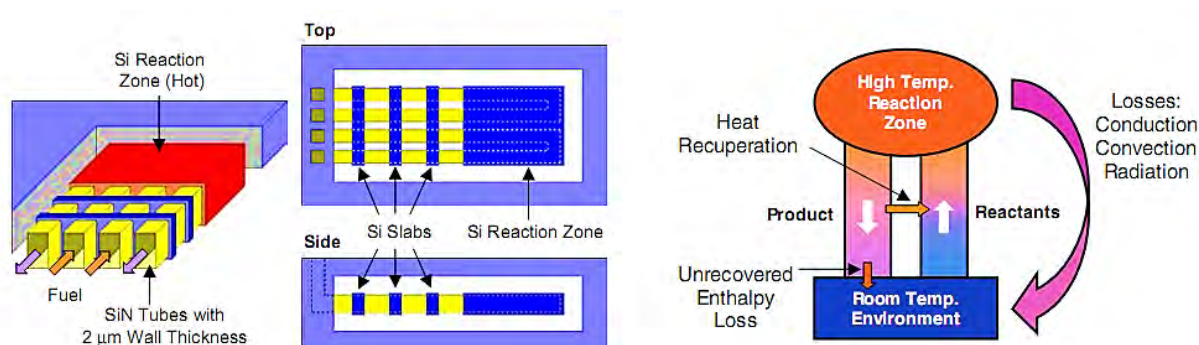


Fig. 2-3 Schematic of the suspended tube microreactor (left) as developed by Arana et al. [44]. In the device, each tube is 200 μm wide and 480 μm high. Major heat loss pathways from the suspended tube microreactor (right). Reprinted (adapted) with permission from [44]. Copyright 2003 IEEE.

Arana et al. [44] developed and investigated an innovative, suspended-tube microchannel reactor for NH_3 decomposition. Fig. 2-3 (left) shows the reactor design, which consists of 4 thin-walled ($2\ \mu\text{m}$) silicon nitride (SiN) tubes. The 4 tubes are essentially two U-shaped fluid channels where NH_3 fuel enters the middle channels and exits on the outer channels in a heat recirculation strategy. The reaction zone is partially encased in silicon for thermal isolation and is 2 mm long. Prior to the Si reaction zone (hot), the SiN tubes are bundled in Si slabs that allow transverse heat transfer between process streams as shown in Fig. 2-3 (right). In this non-reaction length, NH_3 fuel is preheated by the hot product stream.

In their experimental work, 6 sccm of pure NH_3 was fed into an electrically heated suspended-tube microreactor washcoated with an alumina (Al_2O_3)-supported iridium (Ir) catalyst. A conversion of 97% was achieved at atmospheric pressure using an electric power input of 1.8 W ($900\ ^\circ\text{C}$). Having known the power required to achieve high conversion, the researchers developed an integrated reactor-exchanger in which butane combustion on a washcoated $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst supplied the heat to sustain NH_3 decomposition. In this second series of experiments, start-up was initially achieved via electrical heaters and butane combustor performance was examined. Approximately 1.6 W of thermal power was generated by combusting 0.8 sccm of butane in air. Butane combustion was therefore able to sustain NH_3 decomposition in a similar way to electrical heaters. We envision that 97% NH_3 conversion could have been obtained at significantly lower temperatures using more active and less expensive catalysts.

The authors also anticipated a large amount of heat loss from their high-temperature micro-scale device and analyzed the various heat loss pathways (Fig. 2-3: right). Under these temperature conditions, thermal management will always be an important issue. In their microreactor, the high temperature zones were thermally isolated using low thermal conductivity SiN substrate material which also doubled as reactor walls. In addition, their system was

designed similarly to MEMS in that the suspended-tube design allowed for the vacuum packaging to reduce radiation losses. A particularly salient aspect of their design was the integration of a thin-film platinum (Pt) temperature-sensor to detect local temperature profiles within the microreactor. However, the extent to which the thin-film sensor affects the hydrodynamics within the microfluidic channels has not been reported.

Arana et al. [44] also performed a numerical investigation on their reactor design using two-dimensional computation fluid dynamics (CFD) and a heat transfer model to evaluate the effectiveness of the SiN walls in carrying out heat recuperation. Short response times for heat exchange were observed mainly due to the thin SiN walls, signifying sufficient preheating of the NH_3 feed. From a utility perspective, a significant drawback of the suspended-tube microreactor was the considerably high pressure drop even when N_2 was used. We envisage that pressure drop to be even higher when using NH_3 owing to species generation and temperature expansion effects. For small-scale systems, the high compression energy necessary to offset high pressure drop usually reduces overall system efficiency whilst also increasing the balance-of-plant and system costs.

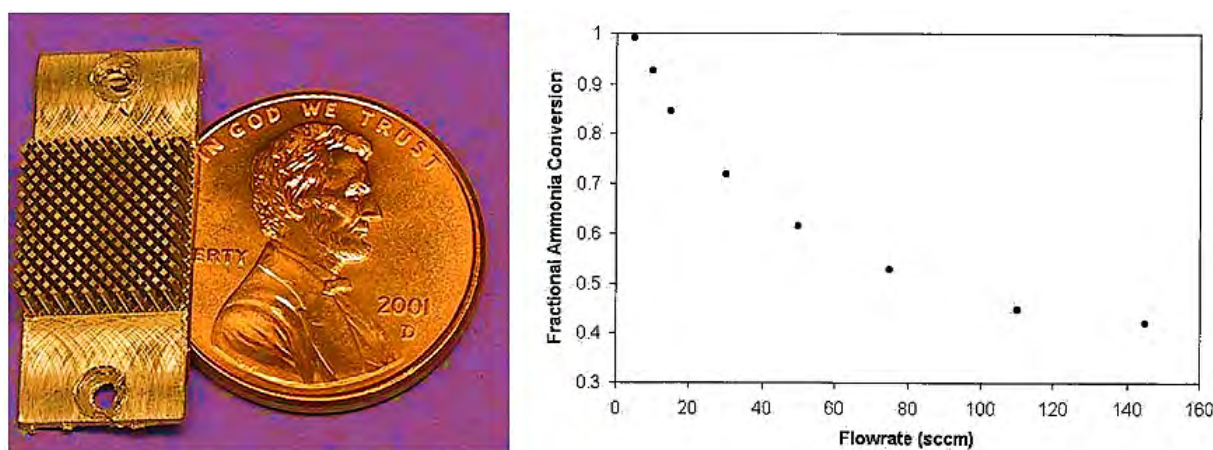


Fig. 2-4 Schematic of a micro-post reactor developed for NH_3 decomposition by Ganley et al. [45] (left). The reactor had a volume of 0.3 cm^3 enclosing 250 square posts each having side length $300 \mu\text{m}$ and height 3 mm . NH_3 conversion as a function of flow rate at 650°C (right). Reprinted (adapted) with permission from [45]. Copyright 2004 John Wiley and Sons.

Ganley et al. [45] developed and tested a micropost reactor (Figure 2-4: left) for H_2 generation via NH_3 decomposition. Unlike the more popular microchannel configuration, a micropost reactor (also referred to as a post microreactor) is composed of multiple static, pillar-like structures that are arranged in the flow channel and covered with catalyst at the surface. Microposts have been reported to have high mixing capacity which often results in enhanced mass transfer to catalyst surface especially under high flow conditions [46,47]. In their work, the researchers fabricated 250 microposts onto an aluminium substrate using electric discharge machining (EDM). Each of these posts was anodized to produce a 60- μm -thick Al_2O_3 support onto which a Ru catalyst was subsequently impregnated. Patermarakis & Pavlidou [48] and Shawaqfeh & Baltus [49], among other authors found that anodization produced Al_2O_3 supports which exhibited superior physical properties compared to conventional catalyst supports. Specifically, anodized Al_2O_3 has high pore size, low variability in pore size, and high surface area even for thick layers exceeding 100 μm .

Given this promising background, one can appreciate the unique preference made by Ganley et al. [45] in developing an anodized alumina post microreactor for NH_3 decomposition. The researchers investigated the operation of their anodized post microreactor in decomposing NH_3 . Their reactor produced H_2 equivalent to 13 W with 85% NH_3 conversion at 650 °C and at a relatively low NH_3 flow rate of 15 sccm. Fig. 2-4 (right) shows that the performance of this post microreactor was far from ideal especially under the high temperature conditions used. The product gas from their microreactor therefore, cannot be directly fed as fuel to a PEM fuel cell unless a considerable mass of adsorbent is used to clean up residual NH_3 or relatively higher temperatures are used.

Ganley et al. [45] concede the necessity of improvements and identified optimization of anodization techniques and reactor geometry as areas of concern, but did not give specifics.

Fig. 2-4 (left) clearly shows a staggered arrangement of the posts. This post configuration has been reported to give poor performance and an in-line post arrangement is often preferred owing to lower pressure drop and higher conversion [50,51]. Also, the surface areas reported in their work were less than those reported in previous similar anodization studies. This may explain the relatively low NH_3 conversion of their post microreactor. Besides fine-tuning anodization techniques, surface area could be increased by reducing the post size while maintaining the same outer reactor dimensions [52]. By doing so, the number of posts per unit volume increases and an enhanced NH_3 conversion is expected. In fact, Deshmukh et al. [53] investigated this post microreactor numerically and revealed that increasing the post density could lead to higher NH_3 conversions at a penalty of high pressure drops (Fig. 2-5).

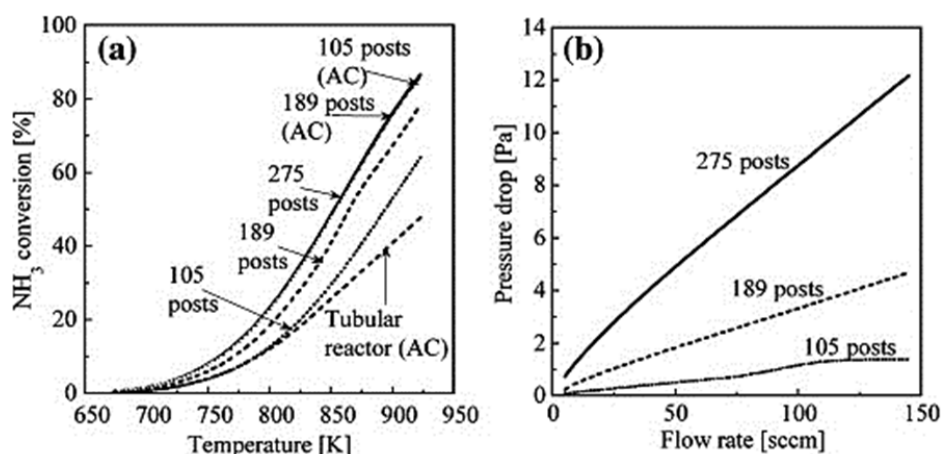


Fig. 2-5 Effect of post density on (a) NH_3 conversion and (b) pressure drop in a post microreactor. Reprinted (adapted) with permission from [53]. Copyright 2004 American Chemical Society.

Deshmukh et al. [53] used CFD simulations to predict and analyze NH_3 decomposition numerically in the experimental anodized aluminium post micro-reactor of Ganley et al. [45]. They developed a microkinetic model from which they concluded that the NH_3 decomposition chemistry in the microreactor was not sufficiently fast to achieve higher conversions. Most important, their CFD simulations showed significant backmixing at the entrance of the post microreactor particularly under slow NH_3 flow conditions. Both these observations assisted in

explaining the moderate NH_3 conversion obtained in the experimental post microreactor. The CFD simulations also investigated flow patterns and revealed that posts generate effective transverse mixing that is unattainable in microchannel reactors, especially under laminar flow conditions. This could have been enough motivation for Ganley et al. [45] and it is possible that Arana et al. [44] incorporated microposts into their suspended-tube microchannel reactor to generate good mixing albeit at the expense of high pressure drop. For reasons mentioned earlier, high pressure drop is undesirable for small-scale applications and so this rare combination of posts and channels may not be desirable. Deshmuck et al. [53] also probed the possible effects of changing the post geometry in the post microreactor. Their results indicated that increasing post density enhanced the NH_3 decomposition rate, while changing the post shape (circular, diamond or triangular) did not have any effect on NH_3 conversion.

In a follow-up publication, Ganley et al.[54] proposed and examined two structured alumina-anodized microreactors for NH_3 decomposition, namely the micropost and microchannel reactors. These reactors were fabricated to have equal surface to volume ratio so as to obtain a basis for fair performance comparison. The post microreactor was similar to their first generation reactor, which they used in a previous study [45] and the microchannel structure had 14 parallel channels each 260 μm wide and 9.2 mm long. The microchannel reactor produced better NH_3 conversion (68%) than the post microreactor (51%) at identical flow and temperature conditions (145 sccm NH_3 and 525 $^\circ\text{C}$). The superior performance of the microchannel configuration was attributed to reduced backmixing, hence their research underlined the channel design as the preferred microreactor structure.

Ganley et al. [54] also investigated the effects of improving the catalyst preparation procedure and reducing channel dimensions on the performance of the microchannel reactor. They found that hydrothermal-thermal treatment of the anodized Al_2O_3 support increased the NH_3 conversion by 4% owing to increased surface area and Ru dispersion. This result confirms

the experimental observations of other authors such as Paternmarakis et al. [55]. They also found an improvement in NH_3 conversion of 10% attributed to incorporating potassium promoter in catalyst preparation. In addition, their experimental results showed that NH_3 conversion increased by 7% when a microreactor with smaller channels (140 μm width) was used. Thus the basic premise that small characteristic length scales reduce mass transfer (diffusion) resistances was confirmed. However, the extent to which pressure drop increased as a result of narrower channels was not investigated. Although the conversion increments following these modifications were modest, their combined effect produced a microreactor that generated H_2 equivalent to 60 W with an NH_3 conversion of 99% at 600 $^\circ\text{C}$ all in a volume of 0.35 cm^3 . At the same NH_3 flow rate of 145 sccm, their first generation experimental post microreactor converted only 42% NH_3 at a slightly higher temperature of 650 $^\circ\text{C}$. However, sustainable operation of the microchannel reactor with respect to material stability may not be possible at this high temperature in view of the melting point of the aluminium substrate. We envisage 550 $^\circ\text{C}$ to be the maximum allowable temperature limit for this reactor, with the obvious penalty of lower NH_3 conversion.

Deshmuck and Vlachos [41] used two-dimensional CFD simulations to explore the operation of a spatially coupled, multifunctional microchannel reactor for H_2 production via NH_3 decomposition. Their microreactor operated countercurrently where homogeneous propane combustion supplied reaction heat to the Ru-catalyzed NH_3 decomposition through a heat-conducting wall (300- μm -thick) separating the different channels. They investigated the effects of wall thermal conductivity and NH_3 flow rate on the operability of their microdevice. NH_3 flow velocities were varied from 0.05 m/s to 0.5 m/s whilst the propane/air mixture velocity was fixed at 0.5 m/s. The wall thermal conductivity was varied from as low as 2 W/m/K to 200 W/m/K.

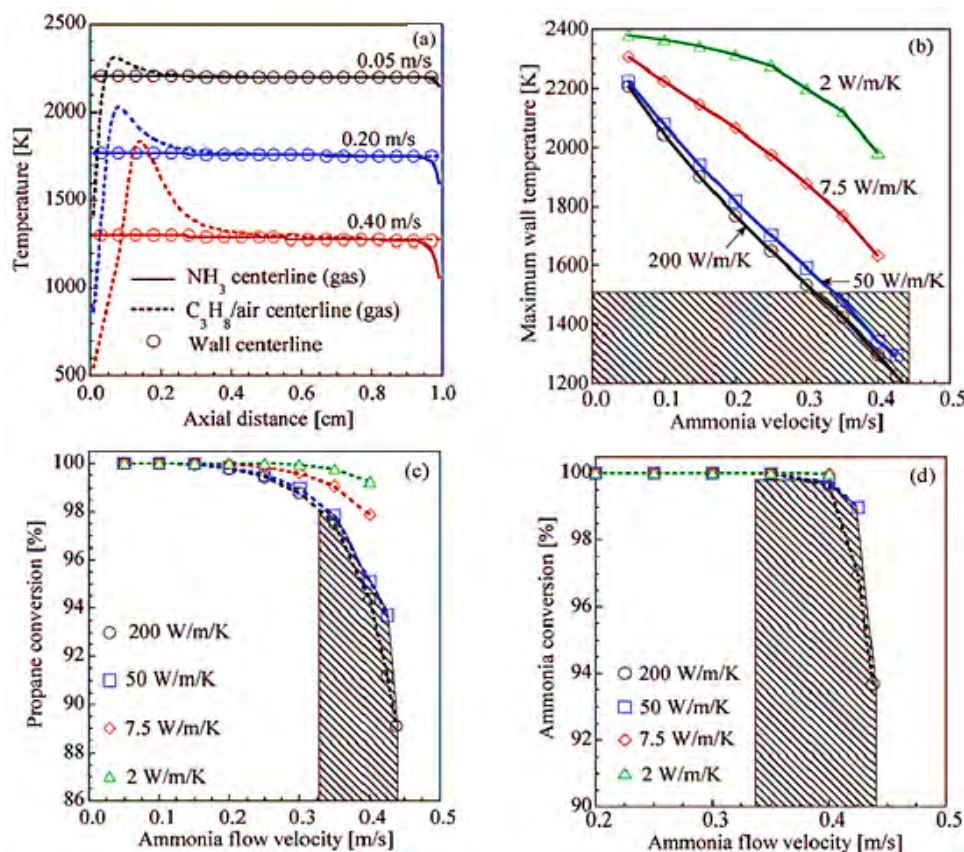


Fig. 2-6(a) Centreline temperature distributions as a function of distance from the C₃H₈/air entrance for various NH₃ inlet flow velocities. (b) Maximum wall temperatures as a function of NH₃ flow velocity and wall thermal conductivity. The shaded area illustrates the materials stability region at 1 500 K. Conversion of C₃H₈ (c) and NH₃ (d) as a function of NH₃ flow velocity for various wall thermal conductivities. The shaded region depicts the operation window delimited by a maximum allowable wall temperature of 1 500 K and the critical NH₃ flow velocity. Reprinted (adapted) with permission from [41]. Copyright 2005 American Chemical Society.

Their simulation investigated the microdevice for a region that could give sustained operation particularly with regard to material stability in terms of the maximum allowable wall temperature and H₂ production rates. The upper operating temperature for their device was determined in consideration of the Tamman temperature limit for a Ru catalyst, 1 500 K [56]. Fig. 2-6(a) reveals that the material stability limit was exceeded at the initial NH₃ flow velocity of 0.05 m/s but faster flows nearer to 0.40 m/s produced a sustainably low device temperature. Fig. 2-6(b) showed that high wall thermal conductivities greater than 50 W/m/K provided sufficient heat recirculation to attain device temperatures below the material stability limit. The low conductivity materials were shown to result in localised hot spots which increased the wall

temperature far beyond the material temperature limit, rendering prolonged device operation impossible.

The CFD simulations also investigated the best operating region for their countercurrent, multifunctional microdevice as shown in Fig. 2-6(c)–(d). Specifically, a critical NH_3 velocity of 0.35 m/s limited the propane conversion to 98% and produced NH_3 conversion >99% in the microreactor. However, higher NH_3 flow velocities above 0.45 m/s were not recommended owing to their high heat removal capacity from the combustion zone, which eventually caused a loss in flame stability and extinction of combustion chemistry. This phenomenon is evident in Fig. 2-6(c), where propane conversion decreases as NH_3 flow increases above the critical velocity. The simulation results also indicated that NH_3 conversion decreased for faster NH_3 flows. Under such conditions, the product gas mixture would require substantial downstream processing before feeding to a PEM fuel cell. In summary, although sustainable operation was demonstrated, the operating conditions were restricted to a very narrow window (0.35–0.40 m/s NH_3 flow), which may be difficult to adhere to in practice.

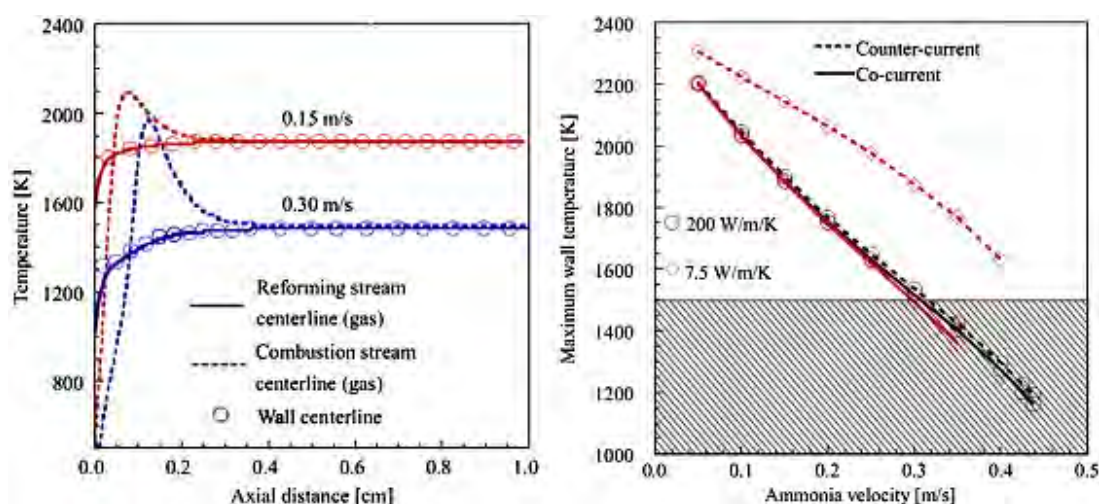


Fig. 2-7 Effect of ammonia flow rate on device temperature in the co-current configuration (left). Comparison of co-current and counter-current configuration in terms of the maximum wall temperature as a function of wall thermal conductivity (right). The shaded region indicates the material stability limit. Reprinted from [57], Copyright 2005, with permission from Elsevier.

In a follow-up communication, Deshmuck and Vlachos [57] sought to expand the operation window of the spatially coupled microreactor device which they investigated in their previous work [41]. Using two-dimensional CFD simulations, they investigated the effect of flow configuration on microdevice operation. Specifically, they compared and contrasted countercurrent and cocurrent spatially coupled microreactor configurations for NH_3 decomposition on the basis of multiple performance criteria, such as device temperature, conversion, and net hydrogen production. The effects of flow configuration were dependent on the competition between axial heat conduction timescale and flow residence time. For highly conductive materials, the heat conduction timescale was found to be shorter than the flow residence time, resulting in fast heat transfer that negated the influence of flow configuration. Consequently, all performance metrics were practically the same for both flow configurations.

For low wall thermal conductivity, the axial heat conduction timescale was longer than flow residence time, signifying slow heat transfer. Fig. 2-7 (right) shows that material stability limits were exceeded for the range of NH_3 flow rates used in countercurrent operation. In contrast, the device temperature in the cocurrent flow configuration remained below the thermal stability limits. In fact, there was no significant difference in wall temperature distribution between materials of low (7.5 W/m/K) and high (200 W/m/K) thermal conductivities. Cocurrent configuration therefore enables use of lower device temperatures and wider spectrum of materials. Also, Fig. 2-7 (left) shows that sustainable device temperatures were attainable at an NH_3 flow rate of 0.3 m/s which is slightly lower than that required for a countercurrently operated microdevice shown in Fig. 2-6(a). For low thermal conductivity however, the cocurrent configuration resulted in slightly lower NH_3 conversion at every axial location within the reaction channel. Despite this slight drawback, the cocurrent microdevice had a much larger operation window in terms of material and device extinction limitations. In summary, their study demonstrated cocurrent operation of the microdevice as the preferred option and

simultaneously presented useful guidelines for the design of future spatially coupled microdevices. This is one instance of engineering importance where the macroscale differ from microscale: in macroscale systems, countercurrent flow is often preferred.

Waghode et al. [58] developed a two-dimensional numerical model to describe the fluid dynamics and heat transfer in catalytic microchannel reactor systems for NH_3 decomposition over a Ni-based non-porous catalyst layer. Their primary focus was to find a numerical technique for dealing with the strongly coupled governing equations and not so much to evaluate optimal design aspects of the microreactor. Sorenson et al. [59] demonstrated NH_3 decomposition in a micro-fabricated silicon reactor of volume 20 μL . Their microreactor contained a barium-promoted Ru catalyst and generated sufficient H_2 to power a 1 W fuel cell at a low temperature of 365 $^\circ\text{C}$. Thus, the H_2 produced was sufficient to power a cell phone. Their experiments were however meant to evaluate the catalyst activity of the barium-promoted Ru relative to the unpromoted Ru. They also used dilute NH_3 hence the reaction proceeds with kinetics that are different to those when using a pure feed.

An essential advantage of their microreactor was the low temperature operation that translates to low insulation volume, which ultimately satisfies the requirement for compactness critical to distributed power generation systems. The details of fabrication of the reactor are published elsewhere [60]. In a follow-up communication, Sorensen et al. [61] used a graphite-supported Ru catalyst promoted with caesium in a microreactor similar to the one used in their previous work [59]. Similar to their previous work, they used dilute NH_3 in their experiments to demonstrate a method to incorporate graphite supports in microreactors for NH_3 decomposition. Considerable NH_3 decomposition rates were reported at temperatures below 227 $^\circ\text{C}$.

Kaisare et al. [62] used a one-dimensional heterogeneous CFD model to study thermal coupling between Ru-catalyzed NH_3 decomposition and Pt-catalyzed C_3H_8 combustion in a

cocurrent microchannel device. Their study is an extension of the work by Deshmuck et al. [57] where the operating window for homogeneous C_3H_8 combustion appeared too narrow for practical use. Specifically, the work of Kaisare et al. [62] proposed catalyzed combustion as an alternative and subsequently performed a qualitative comparison between homogeneous and catalytic C_3H_8 combustion. Their study revealed that stable operation could be achieved for catalytic combustion over a wider range of conditions and at lower temperatures. The wider operating window for catalyzed C_3H_8 combustion allowed for greater device adaptability evidenced by stable operation under various conditions of power tuning. On this basis, the catalytic combustion emerged as the preferable method for supplying heat to the endothermic NH_3 decomposition in multifunctional microchannel devices. Moreover, their work provided fundamental design guidelines with respect to channel gap sizes. They specified open-gap widths $\leq 800\ \mu m$ and $\leq 500\ \mu m$ for the NH_3 decomposition and C_3H_8 combustion channels, respectively. Negligible diffusional resistances were reported for gap widths below the specified limiting dimensions.

Chein et al. [63] used a one-dimensional model to investigate NH_3 decomposition numerically in a cylindrical packed-bed microreactor of length 20 mm and 5 mm radius. In their simulations, the microreactor was filled with spherical Ni–Pt/ Al_2O_3 catalyst particles and operated to a maximum NH_3 flow rate of 500 Nml/min under atmospheric pressure. Their investigations aimed to obtain parameters leading to high NH_3 decomposition efficiency. The microreactor was reported to attain NH_3 conversions >99% at temperatures above 600 °C and slow NH_3 flows less than 0.025 mol/h. The reactor operation at an inlet pressure of 2 bar was not beneficial to NH_3 decomposition as would be expected from thermodynamics. Their results indicated that the porosity and permeability of the packed bed are not parameters of engineering importance, and hence they did not significantly affect the performance of the reactor. Overall, their model provided a good correlation with experimental results obtained

elsewhere [20]. Alagharu et al. [21] developed a mathematical model using reaction engineering principles to analyze process conditions for producing H_2 in a fixed-bed NH_3 decomposition microreactor. Their simulation predicted that NH_3 conversions $>99.5\%$ could be obtained for NH_3 flows of 0.9 mmol/s , provided a heat equivalent of 42 W was available, all to generate a net output power of 100 W in a PEM fuel cell stack. However, the implementation of fixed-bed microreactors has been reported to be difficult in practice due to their higher pressure drops [64] and associated difficulty in maintaining high flow rates [65].

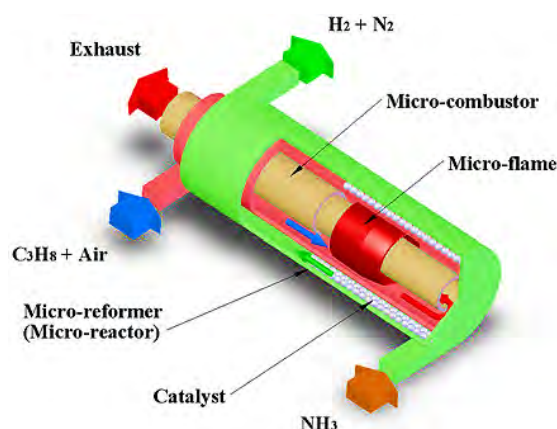


Fig. 2-8 Integrated micro-reformer/micro-combustor system developed by Kim & Kwon [66] for NH_3 decomposition; length: 55 mm ; diameter 16 mm . Reprinted from [66], Copyright 2011, with permission from Elsevier.

Kim and Kwon [66] developed and explored a thermally integrated microreactor that coupled endothermic NH_3 decomposition and homogeneous C_3H_8 combustion. The microreactor consisted of an inner annular-type cylindrical shield (microcombustor) that supplied heat to NH_3 decomposition occurring in an outer annular micro-reformer (Fig. 2-8). This is not an entirely new concept as suggested in ref. [66] but is a variant of the anode off-gas heated cracker prototype developed earlier by Faleschini et al. [67]. Kim and Kwon [66] however, presented a new dimension to the concept by presenting a more in-depth investigation to evaluate the potential of the integrated microreactor system for distributed H_2 generation. In particular, they explored the effects of different operating parameters and various catalyst materials on the performance of the microreforming system. At the optimum conditions defined by C_3H_8 /air inlet

velocity of 3.1 m/s and NH_3 flow rate of 10 Nml/min, Ru-catalyzed NH_3 decomposition produced H_2 corresponding to a thermal power equivalent of 5.4 W at 98% NH_3 conversion and at a system efficiency of 13.7%. We envisage that preheating the NH_3 feed may improve the conversion and H_2 throughput. However, thermal management strategies will need to be evaluated to attain preheating with a minimal increase in reactor volume (maintain device compactness).

In addition, their experimental results also indicated no substantial benefit resulting from increasing the microcombustor inlet velocity above 3.1 m/s, whereas NH_3 flow rates greater than 10 Nml/min resulted in lower conversions owing to small residence times. Besides Ru, other catalysts were also tested with the micro-reformer, namely, $\text{Ni/SiO}_2\text{-Al}_2\text{O}_3$ (65 wt.% Ni) and pure Ir. The Ni-based catalyst gave inferior performance to Ir and Ru at the optimum conditions mentioned above. However, at a higher micro-combustor inlet velocity of 4.1 m/s, corresponding to higher operating temperatures, the NH_3 conversion for the Ni-based system significantly improved (85%) but still remained lower than that obtained using Ru or Ir. Therefore, a microreactor system with a Ni catalyst requires more residual NH_3 downstream processing. Conversely, it is conceivable that a Ni-noble metal bimetallic catalyst may give comparatively equal performances to Ir or Ru as has been observed elsewhere with a Ni-Ir catalyst [68]. If found, such a catalyst would greatly improve prospects for widespread commercial implementation of the integrated microreactor compared to the expensive Ru or Ir system. Because the outer annular micro-reformer resembles a fixed-bed configuration, obtaining pressure drop data (not reported) is essential to determine the operability of the micro-scale system with regard to compression power requirements and overall system efficiency.

Kim et al. [69] investigated the performance of an integrated microcombustor/microreformer similar to the one developed in their previous work [66]. The major difference in their microreactor systems was that their latest system used NH_3 oxidation to supply the heat of

reaction to NH_3 decomposition. To improve the combustion intensity of the NH_3 /air mixture, a split stream of the reformat gas (reformer product) containing H_2 was recycled to the microcombustor. Their work established that the performance of the microreforming system was affected by fuel-equivalence ratio ($\text{NH}_3/\text{O}_2/\text{H}_2$), microcombustor inlet velocity, and H_2 concentration in the reformat gas. They investigated the system performance for two levels of reformat gas H_2 mole fraction: 0.3 and 0.5. The higher H_2 concentration recycle was found to intensify NH_3 oxidation considerably to allow use of lower microcombustor inlet velocities.

In addition, experiments were conducted to investigate the effects of varying the fuel-equivalence ratios of NH_3 - H_2 -air mixtures. Three different fuel mixtures were used: fuel-lean mixture (0.8), stoichiometric mixture (1), and fuel-rich mixture (1.25). The best performance was observed for the stoichiometric mixture and higher reformat H_2 concentration. For the optimized operating condition, the microreformer produced 5.4 W of H_2 equivalent, with 97% NH_3 conversion at an overall system efficiency of 10.4% and a maximum NO_x concentration of 158 ppm in the microcombustor exhaust gas. This performance is comparable to that obtained when propane-air mixtures were used for the microcombustor in the earlier study [66]. It may also be worthwhile to pursue catalytic NH_3 oxidation for the experimental microcombustor/microreformer, given that catalyzed combustion has greater potential to attain thermally stable operation than homogeneous combustion [62].

Chen et al. [51] established a unique numerical scheme to predict the performance of a micropost reactor for producing H_2 fuel for PEM fuel cells via NH_3 decomposition. Instead of applying the commonly used volume-averaging techniques on conservation equations, their simulations were done at pore-scale using the Lattice Boltzmann Method (LBM). The LBM considers flows to be the collective behavior of pseudo-particles residing on a mesoscopic level, and solves the Boltzmann equation using a small number of velocities adapted to a regular grid in space [70]. Thus, pore-scale simulations explicitly resolve the realistic transport phenomena

occurring in porous domain without making any assumptions. Their LBM-based simulations specifically investigated the effect of several operating and geometric parameters on the performance of the post microreactor, namely, NH_3 flow rate, temperature, post size, post insert position, post orientation and post arrangement.

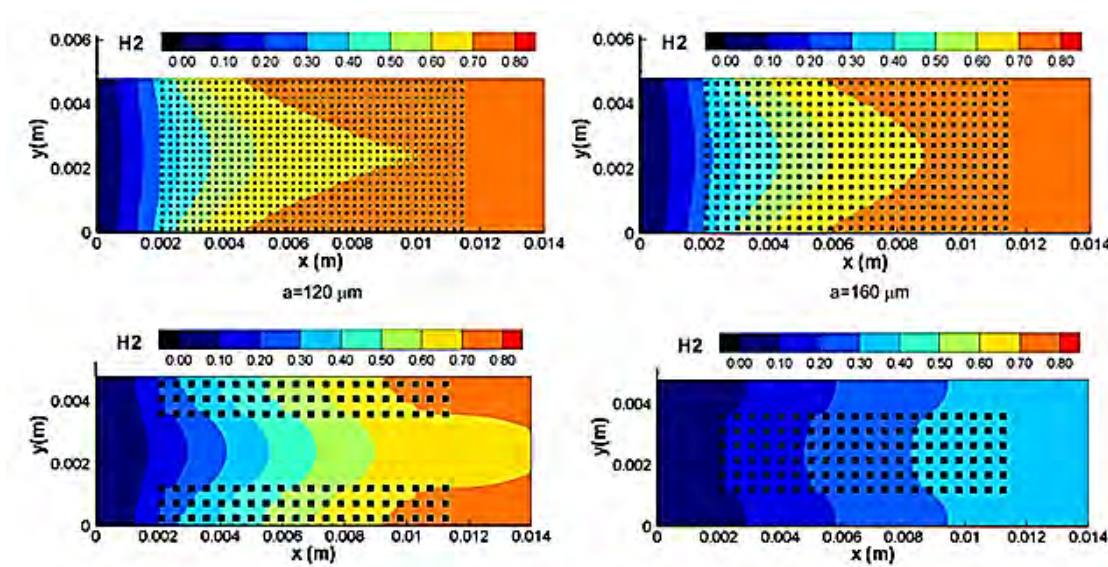


Fig. 2-9 Effect of post size (top) and post insert position (bottom) on micropost reactor hydrogen yield. Reprinted from [51], Copyright 2012, with permission from International Association of Hydrogen Energy.

Ammonia conversions above 95% were obtained only for low NH_3 feed rates below 50 Nml/min and temperatures above 627 °C. Simulation results showed that post size and post position had significant impact on hydrogen yield. As shown in Fig. 2-9 (top), H_2 production is faster when using small posts (120 μm) compared to larger posts (160 μm). Furthermore, the simulations revealed that the best post geometry was achieved when small posts were arranged inline and distributed close to the reactor walls (Fig. 2-9: bottom). It is noteworthy that the simulated post microreactor outperforms the first generation anodized post microreactor investigated by Ganley et al. [45]. Consequently, further work to advance the experimental micropost reactor concept may be done consistent with these design recommendations to achieve the performance breakthrough required for a H_2 supply to PEM fuel cells.

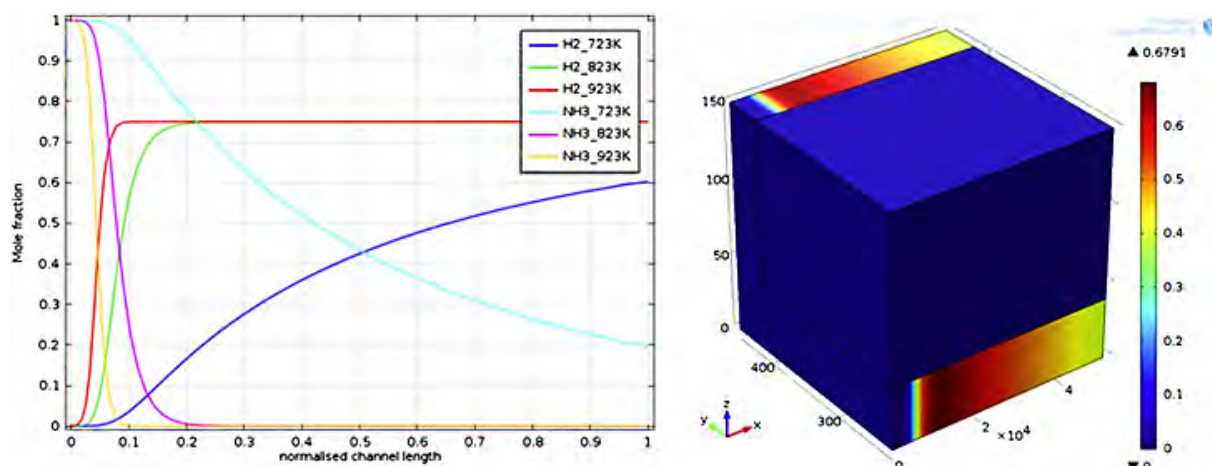


Fig. 2-10 3D CFD simulation results for an ammonia-fuelled microchannel processor: length 5 cm, channel height 150 μm and channel width 450 μm . Species concentration profile along reactor (catalyst) length as a function of wall temperature (left). H₂ formation rate ($\text{kg}/\text{m}^3 \text{ s}$) as a function of reactor position at 773 K wall temperature and an inlet NH₃ velocity of 0.16 m/s (right) [71].

Chiuta et al. [71] used the COMSOL Multiphysics™ simulation tool to model and analyze NH₃ decomposition in a microchannel composite domain consisting of a channel flow-by gap and porous Ni-Pt catalyst layer. Instead of simulating the complete reactor, a single channel was taken to be representative of the entire reactor based on the assumptions of equalized flow distribution and isothermality at steady-state. The 3D CFD model offered possibilities for investigating various transport phenomena and determining the fundamental parameters that affect performance of the microchannel processor. As shown in Fig. 2-10 (left), the reactor wall temperature significantly affected NH₃ conversion efficiency. At the lowest reactor temperature of 723 K, conditions are not favourable to produce H₂ fuel for direct feed to a PEM fuel cell.

At higher-end reaction temperatures however, the reactor yielded NH₃ conversions >99% using only 20% of the channel length. Fig. 2-10 (right) shows H₂ production rate within the catalyst at temperature 773 K and NH₃ inlet velocity of 0.16 m/s. At these conditions, the 3D simulation revealed that maximum H₂ formation rate occurred at about 2 cm from the channel inlet along the catalyst layer. This may be viewed as evidence of the absence of mass-transfer limitations and an appropriately sized channel. However, a detailed analysis based on the

Damköhler number will be needed to confirm this. No reaction occurs in the open channel gap where there is no catalyst. Also, flux magnitudes of different transport mechanisms were investigated and it emerged that convection is predominant in the free-fluid channel whereas molecular diffusion prevails within the porous catalyst layer. The effect of parameters such as NH_3 inlet velocity, permeability and porosity were also evaluated. Permeability and porosity of the porous matrix were shown not to be important engineering parameters. More fundamental work is being done within our research group, details of which will be published in a future communication.

Regatte and Kaisare [72] investigated the spatial thermal coupling of endothermic NH_3 decomposition with catalytic C_3H_8 combustion in a crossflow microreactor using 3D CFD simulations. In part, their study is an extension of previous work by Deshmuck and Vlachos [57] and Kaisare et al. [62]. Specifically, they explored the feasibility of operating the microreactor in a crossflow mode and subsequently compared its performance with a cocurrently-operated microreactor. In the crossflow configuration, their microreactor comprised 5 channels in which NH_3 flow was along the primary axis, and 15 channels for propane/air flow in the transverse direction.

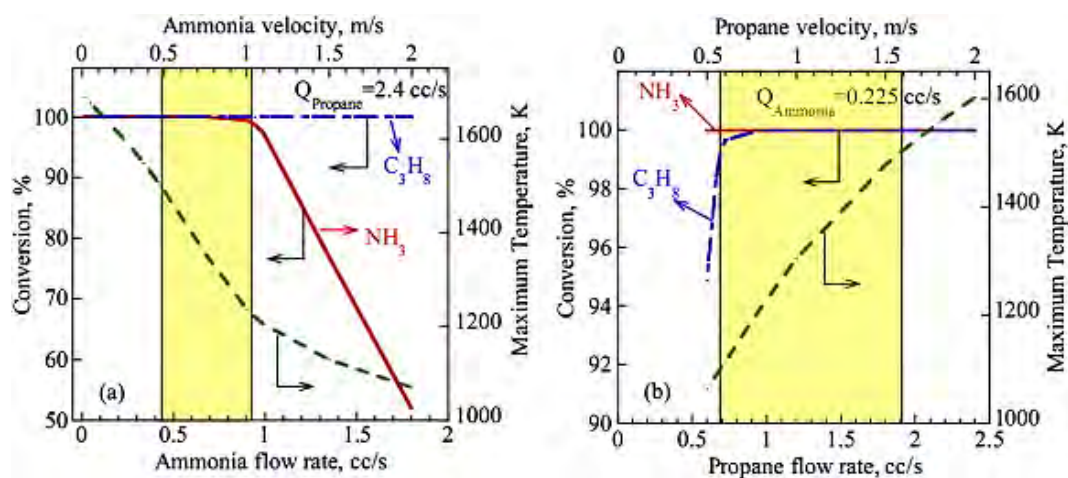


Fig. 2-11 Engineering maps for crossflow (left) and cocurrent (right) multifunctional microreactors for various NH_3 flow rates. The shaded region represents the operating window of at least 99% NH_3 conversion and device temperature below 1 500 K. Reprinted from [72], Copyright 2012, with permission from Elsevier.

Most importantly, engineering maps were constructed to delineate the regions of operation which simultaneously attained 99% NH_3 conversion, while maintaining the reactor temperature below 1 500 K (material stability limit). The results obtained from the CFD simulation showed that sustained device operation of the crossflow microreactor was obtained at low to moderate NH_3 flow rates (Fig. 2-11: left). In contrast, faster NH_3 flows greater than 0.4 cc/s were needed to operate the cocurrent microreactor without violating the material stability and fuel breakthrough (conversion) limits (Fig. 2-11: right). A fundamental design hypothesis resulting from their study is that crossflow microreactors are best suited to low power applications as a result of their ability to sustain operation at very low NH_3 throughput. Conversely, cocurrent microreactors were found to operate at high NH_3 throughput and are therefore suitable for high H_2 production rates with superior energy efficiency.

2.3.2 Monolithic reactors for ammonia decomposition

Monoliths are structures that contain channels (straight, wavy or crimped) in a single block of inert or catalytic material. The channel walls of an inert monolith are usually washcoated or impregnated with catalyst to yield a monolithic reactor. Although the standard shape for monoliths is the honeycomb, they can also be foams or interconnected fibers. Monolith reactors

were initially developed in mid-1970 for the automotive industry and their success as engine emission converters has encouraged researchers to extend their application to other gas-solid reactions. Annually more than 100 000 m³ of monolithic catalysts and catalyst supports are produced worldwide [73]. The channels in monoliths are sized at the microscale, hence it is no surprise that monolithic reactors have similar advantages to microchannel reactors. The main advantages of monolith are low-pressure drop, high-geometric surface, robustness, strength and low weight [74]. In this section, we review the current status of the monolithic reactor technology for distributed H₂ production via NH₃ decomposition.

Christian et al. [75] developed a ceramic microreactor (volume: 1.05 cm³) for NH₃ decomposition using inverted beaded silicon carbide (SiC) monolith with interconnected micropores (0.75–7.2 μm) as catalyst supports. The details of fabrication of the interconnected pore network monoliths are published in their previous work [76]. NH₃ decomposition over a 6%Ru catalyst was reported for temperatures up to 1 000 °C. At the maximum NH₃ flow rate of 36 sccm and temperatures above 700 °C, conversions greater than 99.9% were obtained in the smallest micropore network to produce up to 54 sccm of H₂. With increasing micropore size, higher temperatures were required to attain similar conversions at equal NH₃ flows. Thus, smaller pores produced the highest conversion for a given flow rate owing to high flow residence time. However, small micropores have a dense micropore network and trade-offs between conversion and pressure drop (not reported) are necessary. Although the ceramic microreactors were found to be thermally stable at extreme temperatures, the critical issues surrounding thermal management which are so important for small-scale fuel processing were not addressed in their study.

Lu et al. [77] developed and demonstrated a unique microfibrous composite bed reactor for H₂ generation via NH₃ decomposition at moderate temperatures. The microfibrous structure consisted of 8-μm-diameter interconnected nickel fibres, which entrapped 100–200 μm diameter

porous Al_2O_3 support particulates. Conventional impregnation techniques were used to load the 10 wt.% Ni catalyst as well as 10 wt.% ceria promoter onto the micro-fibrous structure. Their composite reactor produced H_2 (216 sccm) corresponding to 22 W fuel cell power output at an NH_3 feed rate of 145 sccm with a conversion of 99% at 600 °C in a bed volume of 0.5 cm^3 throughout a 100-h continuous test. This is enough power for a laptop computer, and the small reactor volume significantly advances the prospect for practical application. The microfibrinous reactor performance was investigated at different conditions of temperature and NH_3 flow rate. Results indicate that low residual NH_3 (1 ppm) in product gas could be achieved at temperatures between 600–700 °C and low NH_3 flow rates below 150 sccm. The thermally stable micro-fibrous structure is however able to sustain higher temperature operation in order to yield fast H_2 production rate and low residual NH_3 concentrations simultaneously.

In similar work, Liu et al. [78] developed a novel Ni-catalyzed monolithic microfibrinous reactor for NH_3 decomposition to produce CO-free H_2 . Their composite reactor was an upgraded version of that developed by Lu et al. [77]. Instead of entrapping ceria-promoted Ni/ Al_2O_3 catalyst particulates in the Ni fibres, they chemically modified the surface of the Ni fibres with Al_2O_3 and CeO_2 by immersion into an aqueous solution of appropriate nitrite precursors. Their modified microfibrinous composite bed reactor (volume = 0.9 cm^3) attained 99.4% conversion for a 150 sccm NH_3 flow rate at 650 °C to produce H_2 equivalent to 20 W fuel cell power output. At these reactor conditions, the micro-fibrous entrapped composite bed reactor of Lu et al. [77] required half the volume (0.5 cm^3) to give a comparatively better performance (>99.99% NH_3 conversion). Consequently, the entrapped microfibrinous structure demands less residual NH_3 processing than the chemically-modified composite structure. The researchers conceived that the chemical treatment significantly increased the Ni sites but also reduced catalyst site utilization, thereby suppressing activity. Consequently, further improvements are still required to

take advantage of the increased Ni sites and realize the full potential of the chemically modified microreactor structure.

In yet another extension, Liu et al. [79] developed an identical microfibrous composite reactor to that proposed by Lu et al. [77]. However, they used smaller 6- μm -diameter SS-316L microfibers to entrap 100–200- μm -diameter porous Ni/Al₂O₃ catalyst particulates. They consider corrosion-resistant stainless steel fibers an attractive alternative to Ni fibers, which are thought to nitrify and subsequently weaken the microfibrous network especially under a high-temperature (>600 °C) NH₃ environment [79]. Their composite bed reactor was capable of producing 215 sccm H₂ (20 W fuel cell power output) in a bed volume of 0.5 cm³ with NH₃ conversion of 99.5% at 650 °C and 145 sccm NH₃ flow rate. This performance is relatively similar to the one exhibited by the Ni-based structure and underscores stainless steel as a suitable replacement for Ni fiber in microfibrous structures. All the monolithic microfibrous reactors reviewed thus far demonstrated a significant reduction of the overall bed weight and volume compared to a packed bed with 2 mm catalyst pellets. Also, these microfibrous structures were reported to give pressure drops in the order of 59 Pa/mm, which can be considered relatively high compared to those in microchannel reactors [77]. The operational benefits of the microfibrous structures were derived from the large void volume, entirely open structure, large surface-to-volume ratio, high permeability, and high thermal conductivity of the micro-fibrous structure. However, their endeavours do not address the critical issue of thermal management to develop a practical, miniaturized NH₃ decomposition reactor for distributed H₂ production.

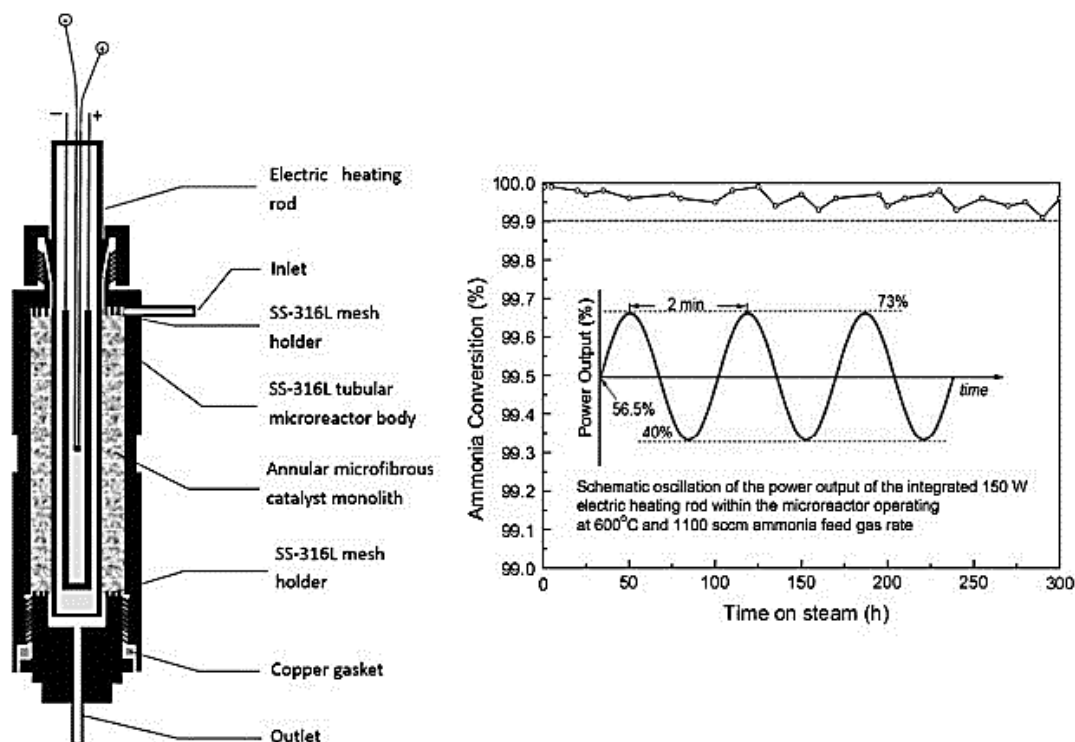


Fig. 2-12 Schematic of the monolithic micro-fibrous microreactor design (left) developed by Wang et al. [13]. Microreactor operability and stability test at 600 °C and 1 100 sccm NH₃ flow rate (right). Reprinted from [13], Copyright 2009, with permission from International Association of Hydrogen Energy.

Wang et al.[13] developed a miniature ammonia cracker (Fig. 2-12: left), with an overall weight of 195 g and volume of 50 cm³ to generate H₂ for portable fuel cell power supply. With due consideration to heat integration, their reactor was an upscale version of the monolithic microfibrous reactor initially proposed in their previous work [77]. The cracker is composed of a SS-316L tube body (16 mm internal diameter and 56 mm length), an electric heating rod (10 mm outer diameter and 50 mm length) and annular slabs of monolithic microfibrous CeO₂-promoted Ni/Al₂O₃ catalysts incorporated within the housings between the heating rod and the inner wall of the tubular body. This microreactor produced 1 650 sccm of H₂ (equivalent to 158 W fuel cell power) with a sustained NH₃ conversion of >99.9% at 600 °C and 1 100 sccm NH₃ feed rate throughout the 300-h test. The power density and energy density of the ammonia cracker were estimated to be 3 160 W/L and 2 150 Wh/ kg, respectively [13].

The insert in Fig. 2-12 (right) shows the instantaneous electrical heater power required to maintain a reactor temperature of 600 °C. The power output of the heating rod oscillated between 40% and 73% of full power (150 W) corresponding to an average heating power of 85 W. Therefore, the net usable power output for such a system will be approximately 73 W. Although the operability of this microreactor was demonstrated, the high electrical power (leading to low system efficiency) of the heating rod may hinder the prospects for practical on-site miniature hydrogen generation for PEM fuel cell power supplies. Therefore, an alternative multifunctional approach in which the system becomes self-sustaining in its energy needs is critical in advancing the micro-fibrous ammonia cracker concept. The heat supply to be used in the multifunctional system should be sufficient to produce at least 85 W, which is the averaged power requirement of the electrical heater rods. For the operating conditions used, the monolithic ammonia cracker produced a relatively low pressure drop of roughly 2 kPa. Consequently, an interesting theory to implementing fixed-bed microreactors while eliminating associated high pressure drops may be to employ a microfibrinous catalyst structure instead of traditional catalyst pellets.

Plana et al. [80] prepared and tested a honeycomb monolithic reactor for distributed H₂ generation via NH₃ decomposition. The cordierite monolith was washcoated with a Ni/Al₂O₃ catalyst. They also prepared a microreactor packed with Ni/Al₂O₃ catalyst pellets for purposes of comparing reactor performance. Their study anticipated that a less expensive Ni catalyst in the form of a structured reactor would have greater activity than expensive Ru. Both reactors could attain nearly complete NH₃ conversion but the monolith reactor did so at a temperature 100 °C less than that which was required by the packed-bed reactor. In fact, the researchers claim 100% NH₃ conversion was observed at 600 °C. Thus, the premise of negligible heat transfer limitations in microchannels was proved in their study. Also, we envisage thermal management will be easier to implement in their monolithic reactor owing to lower operating temperature.

Moreover, near-complete NH_3 conversions are desirable because they minimize the amount of absorbent required to remove residual NH_3 from the reformat gas. Again, the researchers did not investigate any heat integration techniques to make their monolith reactor practical for miniature H_2 generation. As far as we know, this is the only work performed on pure NH_3 decomposition using honeycomb monoliths and results obtained thus far are encouraging. There are other studies that used cordierite monoliths for NH_3 decomposition, but they addressed the cleaning of diluted NH_3 streams which is irrelevant for our review. The work of Ismagilov et al. [81] is an example.

2.3.3 Multifunctional membrane reactors for ammonia decomposition

Multifunctional membrane reactors are a novel reactor engineering concept that integrates reaction, separation and purification of products in the same unit. These reactors are often used to “cheat equilibrium” in applications where equilibrium constraints yield low conversions [82]. As mentioned earlier in this paper, NH_3 decomposition is an equilibrium-limited reaction in which the preferential removal of hydrogen from the reaction zone using a H_2 perm-selective membrane may yield improved NH_3 conversion and enhanced reaction rate. By Le Chatelier’s principle, the membrane exploit is envisaged to increase conversion beyond thermodynamic equilibrium limits, enabling membrane reactors to operate at lower temperatures than conventional tubular reactors [83]. In addition, membrane reactors have been reported to change the manner in which pressure affects the extent of reaction. Specifically, a gas phase reaction which preferentially occurs at low pressure in a conventional tubular reactor can also attain maximum conversion at high pressures in a MCR [84].

The integration of the reaction and product separation into a single unit is a process-intensification strategy that is expected to reduce balance-of-plant and consequently lower the system capital and operational costs. Several researchers have investigated NH_3 decomposition in membrane reactors using dilute NH_3 feeds such as coal gasification streams and purge

streams from NH_3 plants [85–91]. From a fundamentals perspective, these investigations are interesting but the operating conditions and kinetics are different in real systems that generate H_2 for PEM fuel cell application using pure NH_3 . Therefore, we do not attempt to review the whole field of membrane catalytic reactors but restrict ourselves to applications using pure NH_3 .

Zhang et al. [92] developed and evaluated a membrane catalytic reactor (Fig 2-13: left) for generating pure H_2 via NH_3 decomposition for PEM fuel cell applications. The reaction was carried out in the range 698–773 K and 1–5 bar while the NH_3 flow rate varied from 50–400 Nml/min. Their membrane reactor attained higher conversion in comparison to a packed-bed reactor as expected. However, the membrane reactor yielded low H_2 productivity owing to low utilization of the Pd membrane. It is therefore essential for the available membrane area to be fully exploited to ensure enhanced membrane reactor performance in terms of NH_3 conversion and H_2 recovery. Overall, the performance of their membrane reactor was unsatisfactory. Consequently, they developed an alternative exsitu system in which an ammonia cracker was connected to an external Pd membrane purifier. The membrane in the external purifier exhibited superior H_2 productivity and recovery in comparison to that in the membrane reactor. The possible reasons behind the low performance of their membrane reactor will be discussed next in view of their reactor design.

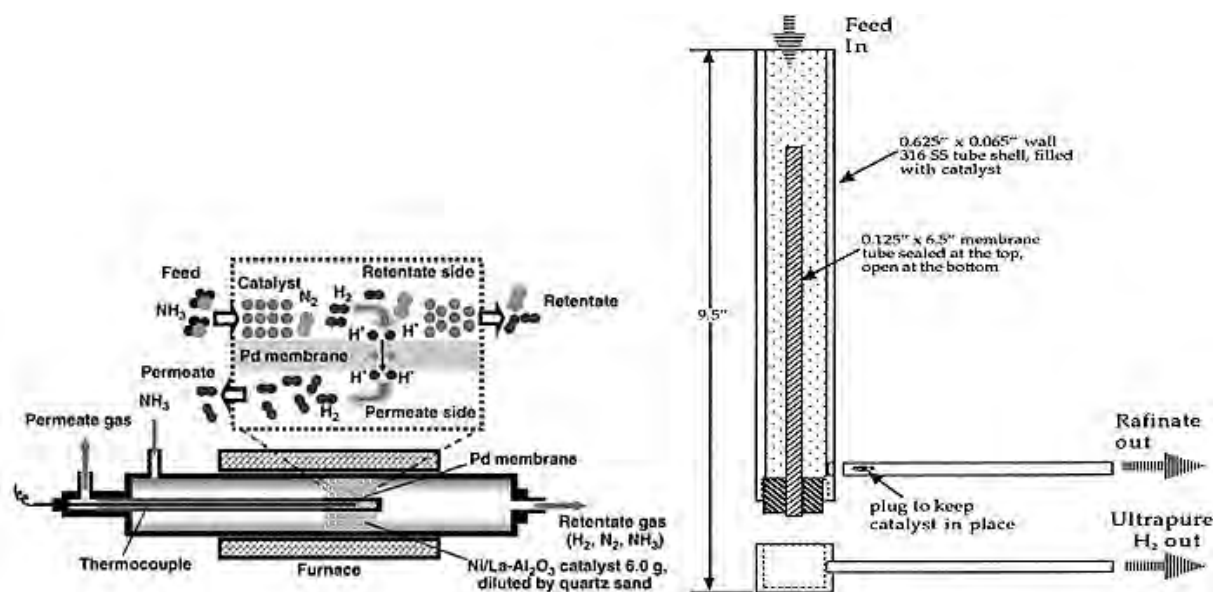


Fig. 2-13 Schematic representation of the packed-bed membrane reactor (left) as used by Zhang et al. [92] for NH₃ decomposition. REB™ research membrane reactor (right) as used by Buxbaum & Lei [93] in steam reforming of methanol experiments. Reprinted from [92, 93], Copyright (2006, 2003), with permission from Elsevier.

First, the placement of the Pd membrane tube at the reactor feed entrance was incorrect so that the retentate H₂ partial pressure was less than the permeate (tube) partial pressure. Consequently, reverse permeation occurred for some distance along the reactor length until the H₂ partial pressure at the reaction side exceeded that at the permeate side. Ideally, the H₂ partial pressure must be greater on the retentate side from the onset to obtain good membrane area utilization. In the integrated system of Zhang et al. [92], this condition was not always present along the membrane length. Therefore, a “breakthrough” allowance gap should have been allocated to yield better performance. The breakthrough length is in effect that gap between NH₃ feed entrance and the membrane tube, which is filled with catalyst. This design feature is apparent in the REB™ membrane research reactor (Fig. 2-13: right) which was used for H₂ generation via steam reforming of methanol [93]. Because NH₃ decomposition is a fast reaction, we expect the breakthrough length be confined to a small reactor length. Second, the countercurrent retentate/permeate flow pattern used in Zhang et al. configuration has been reported to yield lower driving force for permeation compared to a concurrent flow [94].

Garcia-Garcia et al. [90] evaluated the decomposition of NH_3 in a shell and tube type membrane reactor where the catalyst hence the reaction zone was contained inside the membrane tube. Although their work considered dilute NH_3 , it presented an alternative design that researchers may be tempted to adopt for future NH_3 decomposition work using membrane reactors. Below, we review briefly the demerits of such a design. Their system used helium (on shell side) as a sweep gas to increase H_2 permeation by creating sufficient transmembrane pressure difference. The sweep gas however tends to dilute H_2 fuel, which effectively reduces H_2 utilization in the PEM fuel cells. To avoid poor H_2 utilization, the diluted stream needs further purification steps, all this against the logic of process intensification. In addition, membrane reactors of this type have been reported to be less efficient for heat exchange between the reaction zone and the furnace, resulting in poor catalyst exploitation [95]. In view of this, it may be worthwhile to consider using NH_3 feed pressure to create sufficient transmembrane pressure difference and the catalyst remains in the shell side. Yet the extent to which NH_3 feed pressure can be increased needs to be investigated.

Israni et al. [96] performed a numerical and experimental investigation on a packed-bed membrane reactor for NH_3 decomposition. They explored Ni-catalyzed NH_3 decomposition in a packed-bed membrane reactor using (interchangeably) both conventional Pd top-layer (13- μm -thick) and Pd “nanopore” (4- μm -thick) hollow-fibre membranes. The “nanopore” hollow-fibre membrane which they used was a novel product of their previous research [97]. The reaction tests were carried out under the following range of conditions: 500–600 °C; 3–5 bar total retentate (catalyst-side) pressure; 30–700 sccm NH_3 feed rate. For comparison, a conventional packed bed reactor was used for NH_3 decomposition under the same conditions as the membrane reactors. For both membrane types, NH_3 conversion was found to be comparable and 10% higher than in a conventional packed-bed reactor under similar conditions of temperature and retentate pressure. Their innovative “nanopore” membrane however, had

superior H_2 permeation flux and permselectivity as well as more resilience despite its reduced Pd film thickness. Consequently, the Pd “nanopore” configuration has increased chances for commercialization since it produced equal performance with the thicker and therefore more expensive Pd top-layer membrane. Contrary to other membrane reactor studies, NH_3 feed pressure was exclusively assigned to promote H_2 permeation through the membranes. The conversion increased with pressure only for NH_3 feed rates below a critical value of about 230 sccm. High-purity H_2 (>99.2%) was obtained from the membrane reactors at a low H_2 productivity of $2 \text{ mol/m}^3\text{s}$.

Notwithstanding the superior performance of the membrane reactors over the conventional packed-bed reactor, the H_2 purity and productivity obtained were short of the USDOE productivity and purity targets ($50 \text{ mol/m}^3\text{s}$ and 99.99%, respectively) specific for membrane reactors that produce H_2 for PEM fuel cells. The researchers however demonstrated through experiments, that high H_2 productivity could be obtained at the expense of H_2 utilization. In view of this, the membrane reactor was investigated numerically using a two-dimensional pseudo-homogeneous model (1-D heterogeneous model) to identify the various possible operational and design aspects that could lead to an increase in both H_2 productivity and H_2 utilization. Specifically, their model thoroughly scrutinized all the possible physics occurring in reaction and separation of products in the membrane reactor all to isolate the limiting design aspects. The authors determined that radial transport was rate limiting in their system and that any attempt to increase the productivity had to address this constraint. Furthermore, they proposed that smaller reactor diameters could help to offset the radial diffusion limitations on overall membrane reactor performance. This kind of work has been reported to be continuing in their laboratory [96].

Di Carlo et al. [14] studied NH_3 decomposition in a membrane catalytic reactor using 3D CFD simulations. The numerical investigation aimed at establishing reactor conditions at which

maximum H_2 permeation could be obtained and also to determine the extent to which the membrane reactor could improve conversion. For their simulations, their membrane reactor consisted of 7 palladium-coated metal sandwich membranes inside a Ni/Al_2O_3 catalyst bed. The process was simulated for a range of conditions defined by temperatures between 500–600 °C, NH_3 superficial velocity between 1–2 cm/s, and a fixed retentate pressure of 10 bar. Interestingly, the authors had the premonition that lower pressure (<5 bar) would not have been sufficient for H_2 permeation through the membranes. Further investigations may be needed to evaluate their hypothesis given that the reaction kinetics are favoured by low pressure. Their simulation determined the optimal working conditions for the membrane reactor as follows: 550 °C temperature; 10 bar pressure, and 1 cm/s NH_3 inlet flow velocity. At these conditions, an NH_3 conversion of 99.93% was attained, which exceeds the equilibrium conversion at 550 °C (99.92%). Also, their membrane reactor obtained a conversion 18% higher relative to a conventional packed-bed reactor. Experimental verification of the numerical simulations however remain undone.

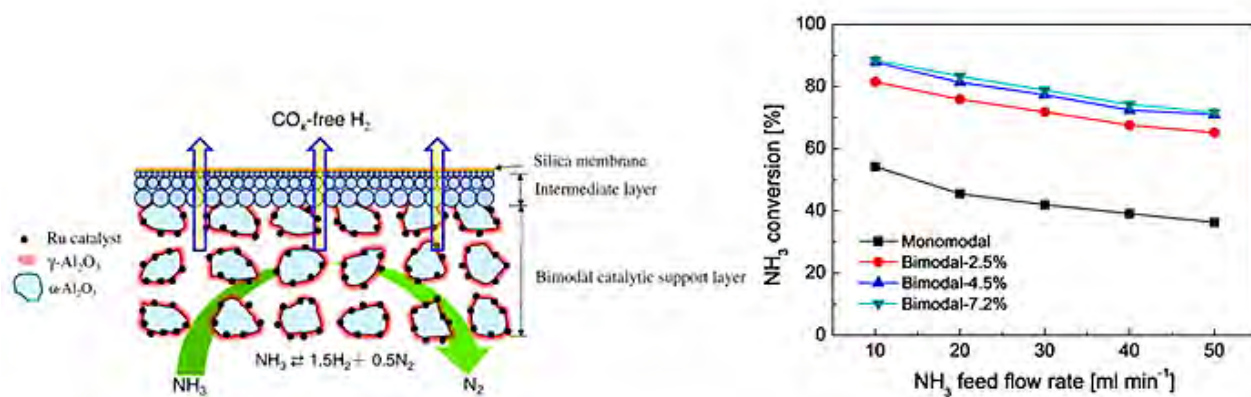


Fig. 2-14 Schematic diagram of the bimodal catalytic membrane reactor for CO_x -free H_2 production via NH_3 decomposition (left). Outer diameter: 10 mm; inner diameter: 8 mm; length: 10 cm. Operational advantages of bimodal catalytic supports over monomodal counterparts for different NH_3 feed rates at 450 °C and 1 bar pressure (right). Reprinted from [98], Copyright 2011, with permission from Elsevier.

Li et al. [98] developed and explored a novel type of membrane reactor for NH_3 decomposition namely the bimodal catalytic membrane reactor (BCMR). The BCMR consisted of a Ru catalyst on a bimodal $\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ support and a H_2 selective silica membrane in a single unit as shown in Fig. 2-14. The details of fabrication are reported in Li et al. [98]. Unlike the packed-bed membrane reactors which have an inert membrane, the BCMR uses an inherently catalytic membrane which eliminates the need for a separate catalytic bed. Consequently, the BCMR has a more compact configuration compared to the conventional membrane reactor [99]. Also, the use of silica membrane layer is expected to reduce the system cost in comparison to membrane reactors that use expensive Pd-membranes.

Ammonia decomposition tests using the BCMR were performed at 450 °C and NH_3 flow rate of 10 Nml/min under atmospheric pressure conditions. At these reactor conditions, a maximum NH_3 conversion of 45% was obtained. However, introducing N_2 sweep gas at 100 Nml/min to the permeate stream significantly enhanced conversion from 45% to 95% owing to enhanced H_2 extraction away from the reaction zone. As discussed earlier in this paper, a membrane reactor using sweep gas has limited practical use for supplying H_2 to PEM fuel cells. In view of this, NH_3 feed pressure ought to be used to increase the transmembrane pressure difference and the performance or stability of the BCMR should be re-evaluated. In addition, the bimodal catalytic membrane separates $\text{H}_2\text{-NH}_3\text{-N}_2$ gas mixtures using molecular sieving effect based on kinetic diameters of the various gas species. Given this mechanism, we envisage some ammonia “creep” to occur through the silica membrane into the permeate stream, hence H_2 purity figures should perhaps have been reported as a figure-of-merit in their work.

Li et al. [100] explored NH_3 decomposition in a pressurized BCMR. Specifically, the following conditions were applied: NH_3 flow rate of 40 Nml/min at 450 °C and reaction feed pressure of 1–3 bar. In addition, no sweep gas was used but the permeate side was operated under vacuum at 5 kPa while the feed (retentate) side pressure was varied to test the effect of NH_3 feed

pressure and therefore H_2 extraction on membrane reactor performance. Enhanced H_2 extraction at high pressures (3 bar) resulted in an increase in NH_3 conversion from 68.8 to 74.4%. Without H_2 extraction, NH_3 conversion decreased from 50.8 to 35.5% in the reactor. Interestingly, the performance of the silica membrane with respect to H_2 permselectivity was reported. The H_2 purity and NH_3 concentration in the permeate stream were 84% and 4.5%, respectively. Thus, the Si membrane is not truly H_2 perm-selective and the “ammonia-ridden” permeate stream cannot be directly fed to a PEM fuel cell. Although the concept has great potential for commercialization, more work needs to be done to optimize the bimodal catalytic support for stricter H_2/NH_3 permeance ratios.

Li et al. [101] performed a numerical and experimental investigation of the BCMR to ascertain the effects of various parameters, such as membrane characteristics and operating conditions on membrane reactor performance. In their study, the mathematical model was formulated and analysis was based on important dimensionless numbers specifically the Damköhler number (Da), permeation number (θ) and membrane selectivity (α_{H_2/NH_3}). Da is a measure of the space velocity which can be increased by using a large catalyst loading or a small NH_3 flow rate. θ is a measure of H_2 extraction and a higher permeation number indicates that more H_2 can be removed from the membrane reactor. These dimensionless numbers were used to quantify the influence of each parameter on membrane reactor performance in terms of NH_3 conversion and H_2 purity. Simulation results (Fig. 2-15) revealed that NH_3 conversion generally increases with increasing Da and θ . This trend was ascribed to the decrease in space velocity as well as the positive effect of H_2 extraction through the membranes. At $Da = 300$, the reaction rate is so high that NH_3 conversion approaches equilibrium value where H_2 extraction (θ) becomes less important.

The H_2 purity in the permeate stream decreased as θ increased from 0.1 to 100 for any value of Da . This trend is more pronounced for $Da = 5$, which corresponds to low catalytic activity

owing to high NH_3 space velocity. Because the silica membrane also permeates NH_3 and N_2 , an increase in θ not only increased H_2 permeation but also reduced H_2 purity. With increasing Da however, there is a slight increase in H_2 purity for a given θ . Consequently, their simulation proposed a design hypothesis that increasing Da cannot be used to improve H_2 purity when using a bimodal catalytic membrane reactor for hydrogen production. The effect of H_2/NH_3 selectivity on NH_3 conversion and H_2 purity was also evaluated at $Da=30$. Generally, the H_2 purity and NH_3 conversion increased with selectivity.

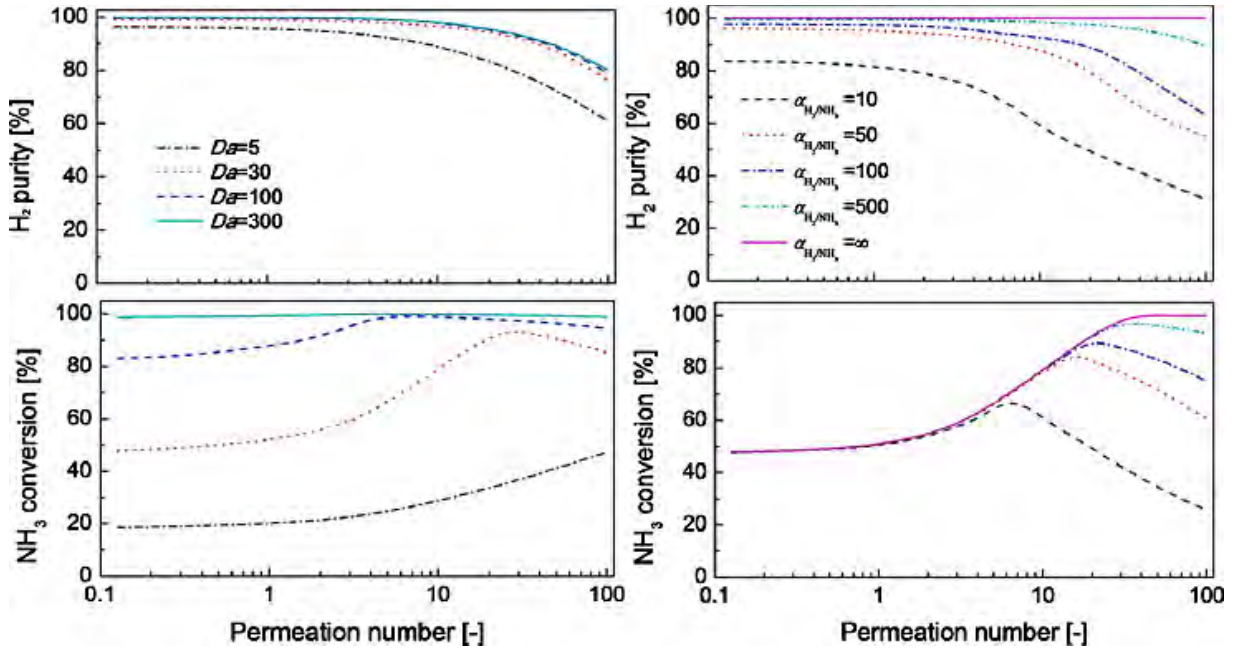


Fig. 2-15 Dependence of NH_3 conversion and H_2 purity on Damköhler number (top), membrane selectivity (bottom), and permeation number as obtained by numerical simulations of Li et al. [101]. The simulations were performed under the following conditions: temperature 723 K; permeate pressure 5 kPa; reactor pressure 1 bar.

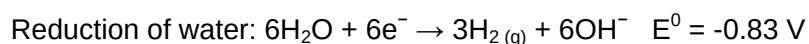
Interestingly, the simulation compared porous silica membranes with conventional Pd membranes ($\alpha_{\text{H}_2/\text{NH}_3} = \infty$), and it emerged that the Pd membrane gave a superior performance (Fig. 2-15: bottom). However, the silica membrane is attractive from a fabrication cost perspective. Overall, the experiment results were in agreement with the simulation model. The researchers also proposed that autothermal operation of the BCMR could be obtained by combustion of retentate stream. The proposed heat integration scheme may still be difficult to

attain in practice because the N₂-rich retentate stream is envisaged to have poor combustibility to supply sufficient heat.

Gormez-Garcia et al. [102] developed methodologies for analysis and design of membrane reactors for removal of NH₃ from exhaust gases generated in the selective catalytic reduction of NO_x. Through their design guidelines, they were able to illustrate performance dynamics and determine the feasibility and operational limits of using membrane reactors for dilute NH₃ decomposition. As mentioned earlier, the performance dynamics of a system decomposing pure ammonia is expected to be different. Hence, a similar systemic approach that provides design guidelines for pure NH₃ decomposition in membrane reactors can also be important. As a starting point, an approach similar to that employed by Prasad et al. [103] may be adopted, where a method is developed for design of experiments using high throughput multi-scale modelling (HTM) to identify important regions for conducting pure NH₃ decomposition experiments in fixed-bed reactors.

2.3.4 Electro-chemical reactors for ammonia decomposition

This section reviews the current status of NH₃ electrolyzers for distributed H₂ production. Ammonia electrolysis can “loosely” be defined as the decomposition of NH₃ by means of an electric current. NH₃ electrolysis is therefore considered an alternative NH₃ decomposition technology in this review. NH₃ electrolysis occurs according to the following half-cell reactions:



At the anode, NH₃ is electro-oxidized whereas alkaline reduction of water occurs at the cathode. The overall electrochemical cell potential, which is essentially the energy needed for the overall NH₃ electrolysis is 0.06 V. Thus, ammonia electrolysis requires 95% less energy than water electrolysis, for which the cell voltage is 1.223 V. Also, NH₃ electrolysis requires ambient

conditions of temperature and pressure unlike endothermic NH_3 decomposition. This particularly makes NH_3 electrolysis attractive for distributed H_2 generation, from a thermal efficiency viewpoint. In addition, H_2 generated from an NH_3 electrolytic cell (AEC) can be used directly in a PEM fuel cell without purification. Despite the advantages, few studies have considered pure NH_3 electrolysis for H_2 production. Of these few studies, none has reported a hydrogen generation rate greater than $1.5 \text{ mmol/min/g}_{\text{cat}}$, which is extremely low.

Vitse et al. [105] explored NH_3 electrolysis in an AEC for hydrogen production. Although the efficiencies obtained were high, a large NH_3 oxidation overpotential was reported to yield slow kinetics at the anode. Follow-up work on electrode catalyst development demonstrated that combinations of Pt and Ir best minimized the overpotential of the electro-oxidation of NH_3 , resulting in a decrease in power consumption during electrolysis [106,107]. Boggs and Botte [104] developed and evaluated an AEC, which used Pt-Ir alloy on the anode and cathode and carbon fiber paper as catalyst support. Most importantly, they coupled the AEC to the PEM fuel cell and managed to obtain some net power (Fig.2-16). They reported improved operation of the electrolytic cell without electrode catalyst deactivation at slightly higher current densities (130 mA/cm^2). Still, the current density obtained was well below the 2200 mA/cm^2 required to achieve the USDOE system cost target of US\$133/kg H_2 [104]. From the synergistic analysis, their system cost was approximately US\$1742/kg H_2 solely due to the mass of precious metal catalyst required. Consequently, electrode catalyst deactivation at high current densities continues to be a difficult challenge to overcome.

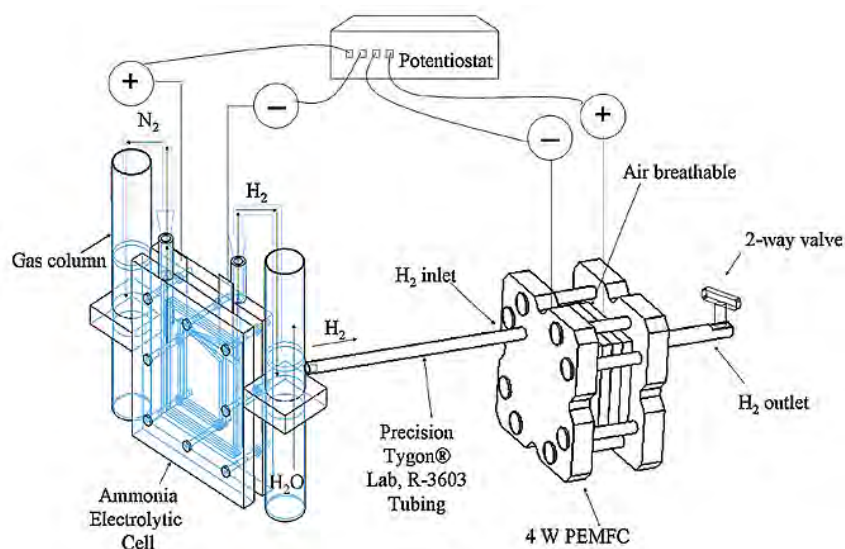


Fig. 2-16 Experimental apparatus for AEC/PEM fuel cell integration at the Electrochemical Engineering Research Laboratory (EERL) as developed by Boggs and Botte [104]. Reprinted from [104], Copyright 2009, with permission from Elsevier.

Current research and development is therefore focused on improving the robustness of the NH₃ electro-oxidation catalyst and improving the slow kinetics at the anode [108–112]. Also, research is slowly shifting to electrolyte development to address these problems. For example, Palaniappan and Botte [114] synthesized a polymer gel electrolyte to replace the common alkaline KOH electrolyte in an AEC. Their experimental results indicated that the polymer gel electrolyte reduced the onset potential for H₂ evolution and consequently increased H₂ production, NH₃ conversion and Faraday efficiency before anode electrocatalysts poisoning occurred. The polymer gel electrolyte therefore allowed a larger operating window for NH₃ electrolysis. However, they concede that the mechanical strength of the polymer gel needs to be improved if it is to replace KOH in NH₃ electrolyzers. Accordingly, NH₃ electrolyzer design remains an under-researched area and scope exists for it to receive much greater attention.

2.4. Discussion and Conclusion

The current paper presented an overview of worldwide research activities over the past decade in the area of development of reactor infrastructure for portable and distributed

hydrogen generation via NH_3 decomposition. In this paper, various aspects were reviewed such as reactor design, operability, power generation capacity and efficiency (conversion and energy). Over the next decade, considerable effort will be needed to advance the various reactor technologies to commercialization on a wide basis. We elucidate the specific details on hurdles to surmount below, but also note that research opportunities are also plentiful in this field of continuing interest. Most of the literature reviewed here was devoted to proof-of-concept studies whilst very few papers had moved past the concept generation stage. Fig. 2-2 showed an average annual publication rate of 3 papers, which is clearly not sufficient to advance ammonia decomposition as a fuel processing technology for distributed H_2 generation. Fig. 2-2 also revealed outright, that exceedingly limited literature is available on integrated numerical-experimental characterization of these reactors. This approach is envisaged to help in the early stages of research and development particularly to attain accurate, optimized reactor designs.

It is clear that microreactors and monolithic reactors appear to be at a relatively more advanced research and development phase than the membrane and electrolytic reactors. Their high conversion efficiency at moderate temperatures has largely contributed to them surpassing some of the USDOE 2015 performance targets, namely; weight, volume, and conversion efficiency. An NH_3 -mediated H_2 economy based on microreactor-monolithic reactors is fast becoming a reality, even for onboard H_2 generation systems. For example, an automobile with a power requirement of 100 kW would require approximately 1 000 monolithic reactors (based on the design of Wang et al. [13]), all to take up a volume of 50 L. Microchannel reactors have smaller volume and weight footprint compared to monoliths, and power scale-up may be achieved easily by numbering up [115] so that they have a greater potential for market penetration. For this reason, microreactors have been the most commonly used reactor technology for NH_3 decomposition as revealed in Fig. 2-2. Membrane reactors are still an attractive concept whose potential as distributed H_2 generators is hindered by the high price of

Pd coupled with low membrane durability and low H₂ flux. Although innovative, thin-film Pd and silica membranes have been developed as alternatives to the expensive Pd membranes; more research is needed to improve their H₂ productivity and purity characteristics. However, the use of steam as sweep gas may work perfectly to increase H₂ productivity. In this configuration, saturated fuel is supplied at the anode side of the PEM fuel cell and there would not be dilution effects such as those found when sweeping with N₂. Meanwhile, NH₃ electrolysis is a relatively new technology whose commercialization potential is greatly hindered by the inability to yield sustainable operation at high current densities and low catalyst loading without catalyst deactivation. Also, much work remains to be done to improve the H₂ generation rate if NH₃ electrolysis is to become competitive with thermocatalytic NH₃ decomposition. In addition, the energy consumption must be reduced in order to produce H₂ at the system cost target of US\$133/kg. Therefore, research must be focused on developing strategies to operate NH₃ electrolyzers at current densities greater than 2 200mA/cm².

Microreactors and a few monolithic reactors have demonstrated outstanding conversion and operability yet they also suffered low energy efficiencies (<15%) for widespread application. There needs to be a tradeoff between start-up time and heat loss with reference to the high surface to volume ratio of microreactors. Kolb [116] reckons that an overall system efficiency of 45% is acceptable for small-scale systems. Mitsos et al. [117] demonstrated that energy efficiency and energy density are not equivalent metrics and portable power generation devices must be designed to maximize energy density rather than energy efficiency. Although energy efficiency is less important for small-scale power generation systems, the topic is too important to be neglected completely. Almost without exception, the literature reviewed here lacks consideration of complete thermal management schemes to achieve efficient overall operation. Thermal management strategies such as spatial thermal coupling and heat recirculation have only been limited to the reactor in isolation of other process components. The realistic

consideration for balance-of-plant has been inadequate and integration among and between components is virtually non-existent in these designs. An efficient thermal integration scheme must consider the overall process including the balance-of-plant components so that the problems of flowsheet design, physical layout, and integration of heat sinks and sources are solved simultaneously. An important starting point would be to perform studies on the coupling of fuel processors to fuel cell. Since the fuel cell is an integral part of a distributed power system, integration studies may assist in providing a complete system analysis and development of suitable start-up and control strategies.

In addition, there has been limited experimental work to investigate these reactors for durability and robustness under dynamic conditions such as frequent start-up and shutdown cycles, which are prevalent in realistic operation. A fair comparison of the reactor technologies is difficult given that these are fundamentally different systems operating at different conditions and having different catalyst inventory and more importantly different figure-of-merits. Overall, we appreciate the wide variety of target applications so that each reactor technology reviewed herein brings its own special attributes in generating hydrogen for distributed power in different settings. Finally, NH_3 decomposition reactor infrastructure will have to be developed mindful of the competition posed by direct ammonia fuel cells (DAFC), which eliminate the need for fuel processing systems to produce hydrogen and are currently being researched worldwide.

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CHAPTER 3: EXPERIMENTAL PERFORMANCE EVALUATION OF AN AMMONIA-FUELLED MICROCHANNEL REFORMER FOR HYDROGEN GENERATION

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Abstract

Microchannel reactors appear attractive as integral parts of fuel processors to generate hydrogen (H₂) for portable and distributed fuel cell applications. The work described in this paper evaluates, characterizes, and demonstrates miniaturized H₂ production in a stand-alone ammonia-fuelled microchannel reformer. The performance of the microchannel reformer was investigated as a function of reaction temperature (450–700 °C) and gas-hourly-space-velocity (6 520–32 600 Nml g_{cat}⁻¹ h⁻¹). The reformer operated in a daily start-up and shut-down (DSS)-like mode for a total 750 h comprising of 125 cycles, all to mimic frequent intermittent operation envisaged for fuel cell systems. The reformer exhibited remarkable operation demonstrating 98.7% NH₃ conversion at 32 600 Nml g_{cat}⁻¹ h⁻¹ and 700 °C to generate an estimated fuel cell power output of 5.7 W_e and power density of 16 kW_e L⁻¹ (based on effective reactor volume). At the same time, reformer operation yielded low pressure drop (<10 Pa mm⁻¹) for all conditions considered. Overall, the microchannel reformer performed sufficiently exceptional to warrant serious consideration in supplying H₂ to fuel cell systems.

Keywords: ammonia decomposition, microchannel reactor, hydrogen generation, fuel cells, performance evaluation

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Chapter 3: Experimental performance evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation

Nomenclature			
ΔH	reaction enthalpy (kJ mol ⁻¹)	DFT	density functional theory
m_{cat}	mass of catalyst in reactor (mg)	GC	gas chromatograph
$\dot{m}_{H_2}$	mass flow rate of hydrogen (kg s ⁻¹)	GHSV	gas-hourly-space-velocity (Nml g _{cat} ⁻¹ h ⁻¹)
$\dot{m}_{NH_3,out}$	mass flow rate of residual ammonia (kg s ⁻¹)	HID	helium ionization detector
$\dot{m}_{NH_3,in}$	mass flow rate of ammonia at inlet (kg s ⁻¹)	IMM	Institut für Mikrotechnik Mainz
$\dot{n}_{T,in}$	total molar flow rate at reactor inlet (mol s ⁻¹)	LHV	low heating value (kJ kg ⁻¹)
$\dot{n}_{T,out}$	total molar flow rate at reactor outlet (mol s ⁻¹)	PEM	polymer electrolyte membrane
P	pressure (Pa)	ppbv	parts per billion volume
P_{eq}	fuel cell power output equivalent (W _e)	ppmv	parts per million volume
Q_e	cartridge heater power requirement (kJ s ⁻¹)	TCD	thermal conductivity detector
Q_{H_2}	molar hydrogen production rate (mol h ⁻¹)	XRD	X-ray diffraction
R	ideal gas constant (82.057 cm ³ atm K ⁻¹ mol ⁻¹)		
T	temperature (K)		
T_r	reactor operating temperature (°C)		
v	volumetric flow rate at inlet (cm ³ s ⁻¹)		
v_c	volume of channel flow-by gap (cm ³)		
v_{H_2}	volumetric hydrogen production rate at outlet (cm ³ h ⁻¹)		
X_{NH_3}	ammonia conversion (%)		
$y_{NH_3,eq}$	residual ammonia mole fraction at equilibrium conversion		
$y_{NH_3,in}$	ammonia mole fraction at reactor inlet		
$y_{NH_3,out}$	residual ammonia mole fraction at reactor outlet		
Y_{H_2}	hydrogen yield (mol g _{cat} ⁻¹ h ⁻¹)		
Greek symbols			
η	reformer energy efficiency (%)		
η_{PEM}	PEM fuel cell energy efficiency (%)		
τ	contact time (ms)		
Θ_{PEM}	PEM fuel cell hydrogen utilization (%)		
$\Phi_{NH_3,eq}$	approach to residual ammonia equilibrium concentration (%)		
Sub-or superscripts			
c	channel		
cat	catalyst		
e	electric		
eq	equivalent		
in	inlet		
out	outlet		
r	reactor		
T	total		
Abbreviations			
AFC	alkaline fuel cell		
DSS	daily start-up and shut-down		

3.1 Introduction

Fuel cells are fast gaining extensive interest for portable and distributed power generation systems. Their exceptional operational characteristics such as high power densities, quiet operation, and inherent ability to generate near-zero pollution make them particularly attractive for a world experiencing simultaneous energy and environmental sustainability challenges [1,2]. The potential for widespread adoption of fuel cell technology however remains subdued owing to several significant techno-economic obstacles. Principally, the low volumetric energy density of hydrogen (H_2) effect storage and transportation difficulties, which create a wide gap in the H_2 supply chain. The existing lack of an adequate infrastructure provokes the need for on-site generation of H_2 via reforming of alternative H_2 carriers in fuel processors. This is considered a promising stop-gap solution at least until problems of H_2 storage and economics are sufficiently resolved [3,4]. Table 3-1 shows the different H_2 -carriers that have adequate energy densities and are available for fuel processing to liberate H_2 .

Table 3-1 Specific and volumetric energy densities of common fuels and power sources [5,6]

Fuel	H_2 content (wt %)	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/L)
Ammonia	17.7	4 318	4 325
Methanol	12.5	6 400	4 600
Methanol (incl. water*)	-	2 040	-
Ethanol	13	7 850	6 100
Ethanol (incl. water*)	-	2 578	-
Hydrogen (700 bar)	100	39 000	1 305
Gasoline	15.8	12 200	9 700
Gasoline (incl. water*)	-	2 140	-
Li-polymer battery	-	110	300

* Including mass of water for steam reforming

Ammonia decomposition as a fuel processing technology has lately been receiving increasing attention for fuel cell applications [7–13]. The position of NH_3 decomposition as an ideal energy vector for the future is accentuated for various reasons. Most importantly, NH_3 is a carbon-free H_2 carrier that has superior H_2 content and gravimetric energy density compared to

alternative carriers (Table 3-1). In addition, NH_3 is an inexpensive fuel (US\$₂₀₁₃580 ton^{-1} [14]) that has an extensive and well-developed manufacturing-distribution infrastructure worldwide to guarantee uninterrupted fuel supply. Also, the availability of NH_3 is incontestable given that the annual global NH_3 production capacity continues to grow by more than 20% [15]. Furthermore, NH_3 decomposition is a simple one-step process (Eq. 1) that has inherent cost benefits in view of reduced mass management challenges and balance-of-plant [13]. On-site power supply at off-grid telecommunication towers is one of the near-term business cases that has great value proposition [13].



The on-site and on-demand H_2 production using small-scale fuel processors is broadly considered key in developing H_2 infrastructure. In fact, miniaturization of the H_2 production system is indispensable especially for portable and distributed power generation using fuel cell technology. In a recent paper, Chiuta et al. [13] reviewed the state-of-the-art reactor technologies for NH_3 decomposition and revealed that microchannel fuel processors had greater potential for market penetration. This is attributed to their compactness (which could provide for easy thermal management) as well as the relative ease of power scale-up achieved simply by numbering-up. Also, their small characteristic length scale (sub-millimetre range) greatly increases the surface-to-volume ratio which leads to enhanced heat and mass transfer characteristics, as well as quick responses to dynamic changes in operating conditions [16–19]. On the contrary, the conventional fixed bed reactor for NH_3 decomposition have size and weight characteristics that can barely serve the needs of a compact fuel cell system [20]. In particular, they require a long time to reach working temperature from cold start-up, and exhibit relatively high external diffusion limitations (film theory) as well as high pressure drop.

Very little work is however reported in literature on experimental investigation of microchannel fuel processors for NH_3 decomposition. Over the past decade, literature reports only five experimental studies using microchannel reactors [13]. Powell and co-workers [21,22] developed a compact system (based on the microchannel reactor design), but their work focused more on system integration than on evaluation and analysis of reactor performance. Similarly, Arana et al. [23] emphasised on evaluating heat recirculation in their thermally-coupled microchannel reactor. Ganley et al [24] examined and compared two microreactor designs for NH_3 decomposition, and identified the microchannel structure to be the preferred design. Sorenson et al. [25] and Sorensen et al. [26] performed experiments on NH_3 decomposition in a microchannel reactor where the main focus was on evaluating the effects of barium and caesium promoters on a ruthenium catalyst, respectively.

Against this background, enormous opportunities exist to advance fundamental NH_3 decomposition studies in microchannel reactors for the purposes of fuel cell applications. In this paper, the reformer performance was evaluated by investigating the effect of reactor temperature and space velocity on key performance parameters vis-à-vis NH_3 conversion, residual NH_3 concentration, H_2 production rate, and pressure drop. Particular attention was devoted to defining operating conditions that minimise residual NH_3 in reformat gas, while producing H_2 at a satisfactory rate. The overall approach adopted for this study involved experimental evaluation of the microchannel reformer and identified the best operating conditions of the stand-alone unit before considering other potentially confounding problems such as thermal-coupling. The results of this paper may be considered design targets for the future construction of a complete NH_3 fuel processor in which the stand-alone reformer analysed herein forms an integral part. The purpose of this paper was to evaluate, characterize, and demonstrate miniaturized H_2 production in an ammonia-fuelled microchannel reactor.

3.2. Experimental

3.2.1 Microchannel reactor design

The microchannel reactor (Fig.3-1) was designed and constructed in collaboration with IMM (Mainz, Germany). The microchannels were fabricated on a SS314 stainless steel (German steel classification 1.4841) substrate having a thickness of 2 mm. Wet chemical etching using aqueous ferric chloride solution as an etchant was used to engrave the microchannels onto the substrate according to the detailed procedure given elsewhere [27, 28].

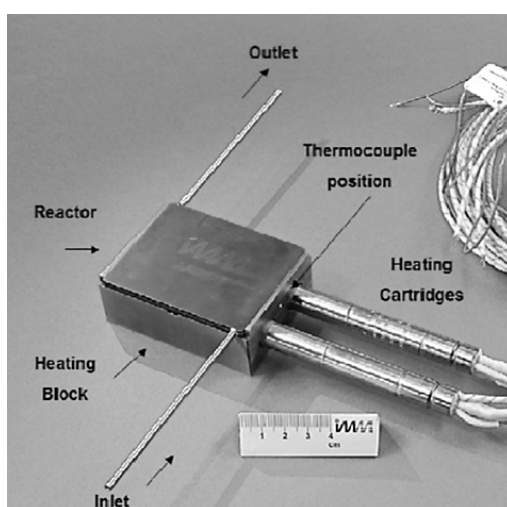


Fig. 3-1 Depictions of the reactor with laser-welded inlet/outlet tubes, heating block and electric heater cartridges

The plate consisted of 80 microchannels (depth = 150 μm , width = 450 μm , width of fin between channels = 250 μm , and length = 50 mm), along with right-angled triangular header and footer manifolds (Fig.3-2:a–b) at the inlet and outlet ends of the channels, respectively. The geometrical design of these manifolds was based on the guidelines given by Commenge et al. [29]. Zeng et al. [30] also investigated the effect of the manifold shape on fluid distribution among microchannels, and concluded that microchannel plates with right-angled manifolds enabled a narrow velocity distribution (fluid flow equipartition). An equally-sized platelet without channels but with inlet and outlet manifolds was also fabricated (Fig.3-2b). This was subsequently laser welded on top of the washcoated channel-engraved platelet to complete the microchannel reformer. Inlet and outlet piping (also stainless steel) was laser welded to the

reactor body. A reactor casing was also manufactured which housed two cartridge heaters (Watlow FIREROD®) with integrated thermocouples for reactor temperature control. In addition, 2 small bores (1 mm diameter) were drilled into the heating block so that thermocouples were positioned right next to the reactor wall.

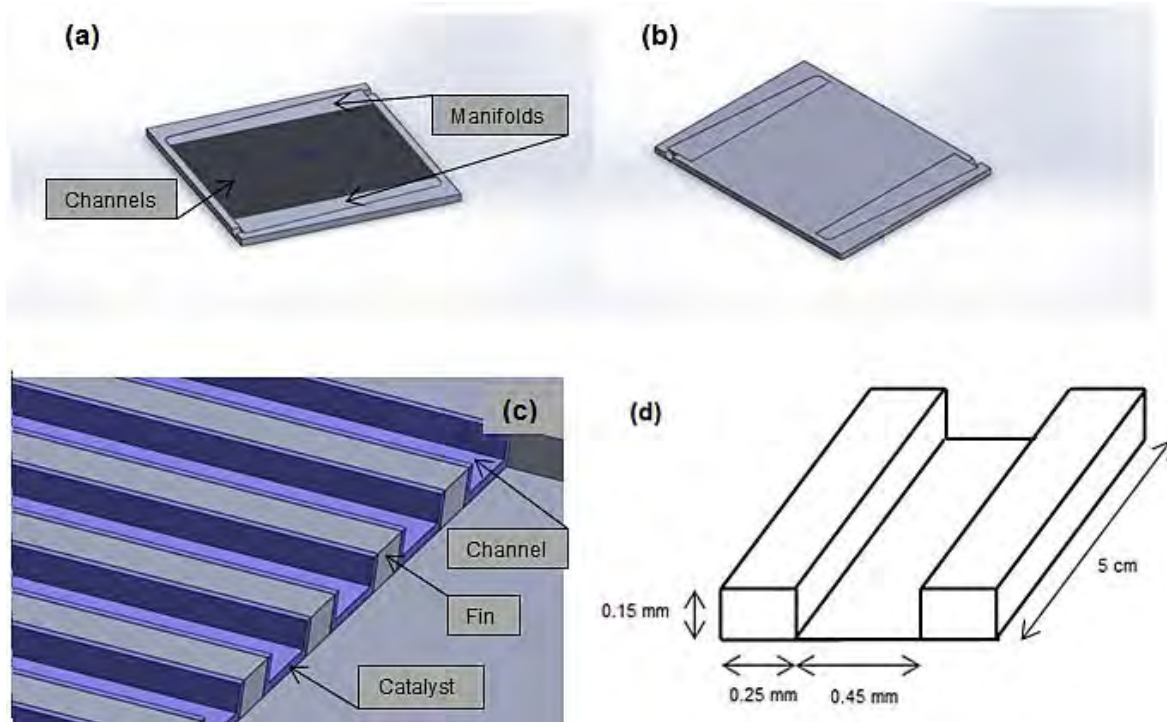


Fig. 3-2 Depictions of (a) microstructured platelet showing 80 channels and inlet and outlet fluid distribution manifolds (b) platelet with only manifolds engraved and for laser-welding on microstructured platelet to complete the microchannel reactor (c) zoomed view of first 5 channels from the far-side wall of the metal substrate (d) cutaway schematic of an uncoated channel

3.2.2 Catalyst preparation

A commercial Ni-Pt/ Al_2O_3 (ActiSorb® O6: formerly G43-A, United Catalyst) catalyst supplied by Sud-Chemie AG (now Clariant) was chosen for this study. Hansgen et al. [31] used microkinetic models combined with DFT data and temperature-programmed desorption tests to conclude that a Ni-Pt bimetallic catalyst is suitable for NH_3 decomposition. ActiSorb® O6 catalyst has not been used anywhere for purposes of evaluating the reformer performance in NH_3 decomposition for H_2 generation. The loading of the catalyst was determined using XRD (GEO XRD & XRF lab, North-West University) and found to be 4.7% NiO and 0.1% PtO on $\gamma\text{-Al}_2\text{O}_3$.

For the microchannel reformer, the catalyst was introduced into the microchannels by a sequential washcoating, drying and calcination process described elsewhere [32–34]. A layer thickness of 40 μm was achieved for the catalyst washcoat. The microchannel reformer plate carried a total 92 mg of catalyst washcoat. The coating demonstrated good adhesion and impact resistance when exposed to a series of vibration and impact tests to mimic rough handling expected in real operation [34].

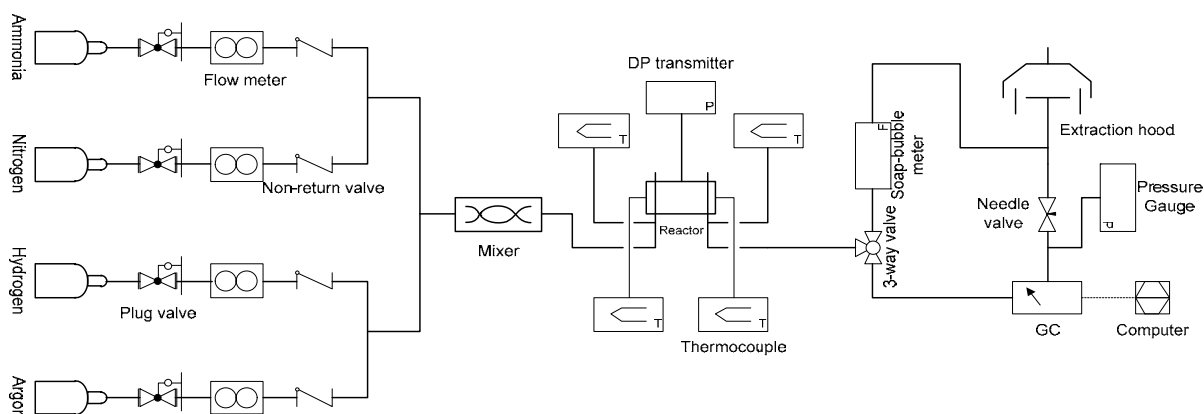


Fig. 3-3 Experimental apparatus for ammonia decomposition

3.2.3 Experimental apparatus and procedure

3.2.3.1 Description of experimental reactor system

The experimental test apparatus (Fig.3-3) comprised of three sections namely feed preparation, reaction, and product analysis. Anhydrous NH_3 (99.99% min.), H_2 (99.99% min.), and Ar were regulated by the respective Brooks SLA5850 thermal mass flow controllers. The heating to the microchannel reactor (thermally insulated) was provided by two cartridge heaters regulated by a temperature controller. The reactor temperature was measured by two K-type thermocouples inserted at opposite ends (axial) into reactor housing. Two additional K-type thermocouples were placed at inlet and outlet of the reformer. An AT9000 DP pressure

transmitter (Model GTX31D) capable of Pa-range accuracy was connected to the reactor inlet and outlet tubing to measure the reactor pressure drop at the different operating conditions. The flow rate of the reformat gas was measured by a soap-bubble meter.

The composition of the reformat gas was analyzed downstream of the reformer by an online SRI8610C GC equipped with two TCDs, one HID, two Molecular Sieve 13X columns (1.8 m and 0.9 m), and one HayeSep D column (1.8 m). The GC was configured in a manner that allowed simultaneous analysis of all species present in the reformat gas. H_2 and N_2 (products) mole fractions were determined from the channel consisting of the shorter molecular sieve column and a TCD. This channel used Ar as the carrier gas. Meanwhile, unconverted (residual) NH_3 was determined from a different channel consisting of the longer molecular sieve column in series with the HayeSep D column. For this channel, two detectors namely the TCD and HID were used in series with He as carrier gas. The strategy was to “delay” elution of NH_3 by reversing the column sequence using a stop-flow solenoid while flow direction remains the same.

3.2.3.2 Description of experimental procedure

Prior to the experiments, the microchannel reformer was heated in Ar (75 Nml min^{-1}) to 400°C for 30 min. After that, the catalyst was reduced at 700°C under flowing H_2 (55 Nml min^{-1}) for 2 h [35]. At the end of the pre-treatment, the system was adjusted to the desired reaction temperature under Ar flow. Reformer operating conditions including reaction temperature and GHSV were varied at atmospheric pressure to investigate the optimum reaction condition defined as giving the best performance. The average wall temperature measured by two thermocouples inserted into the reactor housing was taken as the reactor temperature. Preliminary measurements showed temperature deviation of $<3^\circ\text{C}$ between the thermocouples, demonstrating isothermal operation. Initial experiments revealed very low NH_3 conversions for reaction temperature less than 500°C . In fact, the light-off temperature was

observed at 450 °C. Consequently, the microchannel reformer was investigated only for higher reaction temperatures (550–700°C) that produced substantial NH₃ conversion. The reformer feed consisted of pure NH₃, with GHSV in the range 6 520–32 600 Nml g_{cat}⁻¹ h⁻¹ corresponding to inlet flow rates of 10–50 Nml min⁻¹ and contact times (τ) of 975–195 ms. Again, initial experiments showed that reformer operation at contact times less than 195 ms resulted in increased residual NH₃ in the reformat, whilst H₂ production rates for contact times more than 975 ms were considered too slow.

Since DSS operations are envisaged for applications of fuel cell systems, experiments were essentially performed in a DSS-like mode, with the reactor started up in the morning then operating for 6 h before shut-down. Experiments were conducted for a total 750 h comprising of 125 DSS operating cycles. Also, experiments were conducted one parameter at a time while keeping the others constant. Pertinent runs were made both at highest and lowest space velocities. A performance durability and stability test was conducted on the reformer over a 150-h continuous operation. This test was performed after the reformer had endured approximately 750 h of DSS-like operation (>125 cycles). A reaction temperature of 650 °C and GHSV of 19 560 Nml g_{cat}⁻¹ h⁻¹ were chosen for the stability test. If at all possible, the catalyst need not be deactivating with time on stream. The SRI8610 GC provided quantitative data for the product species (N₂ and H₂) and residual NH₃. Data collection was scheduled at 30 min intervals for 6 h. Analysis of a reformat sample took 10 min, and 12 data points taken over the 6 h were averaged to give one experimental data point. The component mass balances were obtained for each experiment and found to be accurate within 10%. Further, experiments were repeated on different days and data were reproducible within a relative error of 1%.

3.2.4 Reformer performance parameters

The important performance parameters used were NH₃ conversion, residual NH₃ concentration, H₂ yield, fuel cell power output equivalent, approach to residual NH₃ equilibrium

concentration, and pressure drop. The raw data from the experiments were used to calculate the performance metrics, which are defined by Eq. 2–7:

$$X_{NH_3} = \frac{n_{T,in}y_{NH_3,in} - n_{T,out}y_{NH_3,out}}{n_{T,in}y_{NH_3,in}} \times 100\% \quad (2)$$

$$Y_{H_2} = \frac{\dot{Q}_{H_2}}{m_{cat}} = \frac{P\dot{v}_{H_2}}{RTm_{cat}} \quad (3)$$

$$P_{eq} = \eta_{PEM} \theta_{PEM} \dot{Q}_{H_2} LHV_{H_2} \quad (4)$$

The product of the last two terms in Eq.4 represents the thermal wattage of H_2 produced [2, 36].

$$\tau = \frac{v_c}{\dot{v}} \quad (5)$$

$$\varphi_{NH_3,eq} = \frac{y_{NH_3,eq}}{y_{NH_3,out}} \times 100\% \quad (6)$$

Equilibrium NH_3 conversion values were calculated at different temperatures using HSC Chemistry 7 software via the Gibbs free energy minimization method [13]. The reformer energy efficiency (η) was also defined as the lower combustion enthalpy rate of the product stream divided by the sum of the lower combustion enthalpy rate of the feed stream and the electric energy provided by cartridge heaters [37].

$$\eta = \frac{(LHV_{H_2} \times \dot{m}_{H_2}) + (LHV_{NH_3} \times \dot{m}_{NH_3,out})}{(LHV_{NH_3} \times \dot{m}_{NH_3,in}) + Q_e} \quad (7)$$

3.3 Results and Discussion

This section was structured in sub-sections as follows: The stability of the reformer performance was discussed upfront in Section 3.1. Then, the effect of reactor operating temperature on NH_3 decomposition was established in Section 3.2. Subsequently, the reformer

performance for NH_3 decomposition was investigated as a function of space velocity in Section 3.3. In Section 3.4, H_2 production characteristics of the reformer were discussed. Then, Section 3.5 gave a concise analysis of the pressure drop characteristics of the ammonia-fuelled microchannel reformer. The best operating conditions for the microchannel reformer were discussed in Section 3.6. Finally, the performance obtained was compared with that of other micro-structured reactors reported in literature for pure NH_3 decomposition.

3.3.1 Performance stability of microchannel reformer

For the performance stability test, NH_3 conversion and residual NH_3 in the reformat gas were monitored as a function of time as shown in Fig. 3-4. The results shown in Fig. 3-4 (left) show that the NH_3 conversion remained constant at 93.8 (± 0.2 %). Also, the reformat composition was shown to yield an H_2/N_2 molar ratio of 2.9, which is very close to the stoichiometric value of 3. In Fig.3-4 (right), the residual NH_3 in the H_2 -rich reformat varied between 2.3–2.7% throughout the entire 150-h test. Also, the microchannel reformer kept its mechanical stability and shape. Overall, the reformer demonstrated its long-term performance durability, and showed that frequent start-up and shut-down operation did not affect its stability.

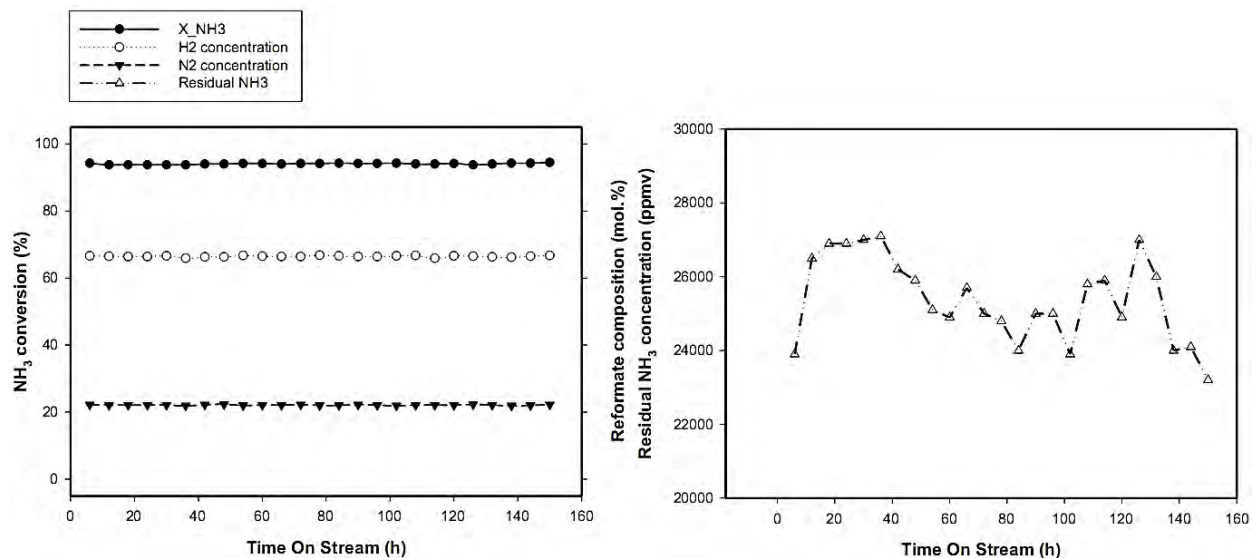


Fig. 3-4 Performance durability of microchannel reformer in NH_3 decomposition over ActiSorb® O6 catalyst; NH_3 conversion (left) and residual NH_3 in reformat (right) as a function of time-on-stream. Experimental conditions: $T_r = 650$ °C, NH_3 flow rate = 30 Nml min^{-1} ($\text{GHSV} = 19\,560 \text{ Nml g}_{\text{cat}}^{-1} \text{ h}^{-1}$)

3.3.2 Effect of reformer temperature on ammonia decomposition

In Fig.3-5, the influence of reaction temperature on NH_3 conversion and residual NH_3 concentration is established at three levels of space velocities. NH_3 conversion increased remarkably with increase in reactor temperature (Fig. 3-5: left). To give perspective to the current discussions, Fig. 3-5 (left) compares equilibrium and experimental NH_3 conversions. Equilibrium calculations render values of 99.82–99.95% for reaction temperatures 550–700 °C, respectively. Evidently, reformer operation at temperatures less than 650 °C was unrestricted by thermodynamics for the highest and intermediate GHSV. On the contrary, the reaction visibly became more equilibrium-limited for these space velocities and for reaction temperature above 650 °C. However, thermodynamic limitations appeared to set in at relatively low temperatures for the lowest GHSV where higher NH_3 conversions were attained. For this space velocity, the increase in NH_3 conversion was insignificant (99.28 to 99.30%) when the reactor temperature increased from 650 °C to 700 °C (Fig. 3-5: left). More interesting, NH_3 conversion differed marginally (98.7–99.3%) for all GHSV at 700 °C, indicating the existence of strong thermodynamic limitations at the highest reaction temperature.

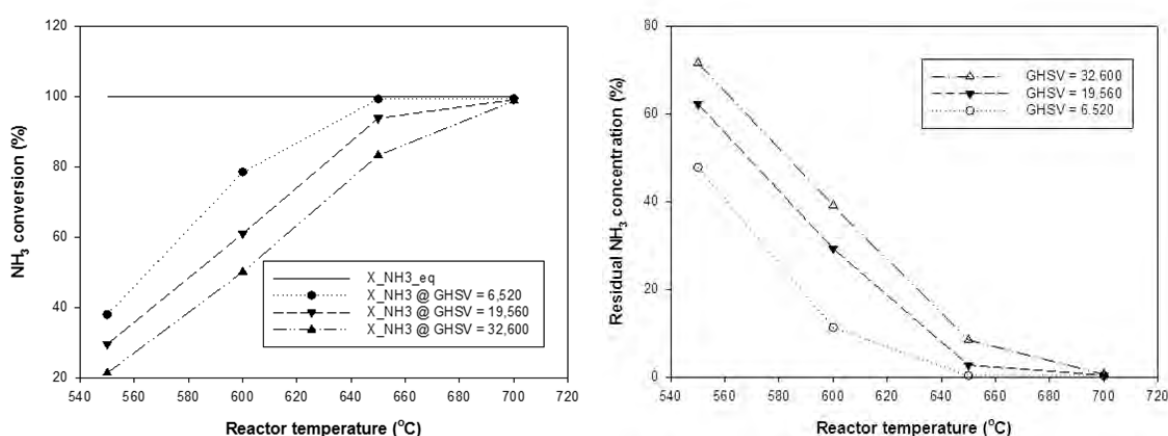


Fig. 3-5 Effect of reaction temperature on NH_3 conversion (left) and residual NH_3 concentration (right). Experimental conditions: $T_r = 550\text{--}700$ °C, atmospheric pressure, GHSV = 6 520, 19 560 and 32 600 $\text{Nml g}_{\text{cat}}^{-1} \text{h}^{-1}$.

The effect of reaction temperature on the residual NH_3 concentration is shown in Fig.3-5 (right). Generally, elevated reactor temperatures inclined to produce reformat gas with less residual NH_3 concentrations. The minimum residual NH_3 (2 600 ppmv) was produced at the highest temperature (700 °C) and lowest space velocity (6 520 $\text{Nml g}_{\text{cat}}^{-1} \text{h}^{-1}$). This is shown more clearly in Figures 3-6 and 3-7. For PEM fuel cells, even a trace of NH_3 (>100 ppbv) in the reformat gas can lower the fuel cell performance significantly [38, 39]. The residual NH_3 concentration in the reformat gas is therefore a critical factor to consider in evaluating the performance of the microchannel reformer. The sections 3.3 and 3.6 discussed this central operational aspect in more detail.

3.3.3 Effect of space velocity on ammonia decomposition

The results presented in Fig.3-6 (left) show that the NH_3 conversion decreases with increasing space velocity. This may be ascribed to the short contact times that limit the extent to which the reaction occurs on the catalyst layer. The trend is considerably more apparent at lower reaction temperature (600 °C). For that reason, the microchannel reformer must be operated at reaction temperature above 650 °C. The study therefore investigated the residual NH_3 concentration as a function of space velocity at two reaction temperatures of interest (650 and 700 °C).

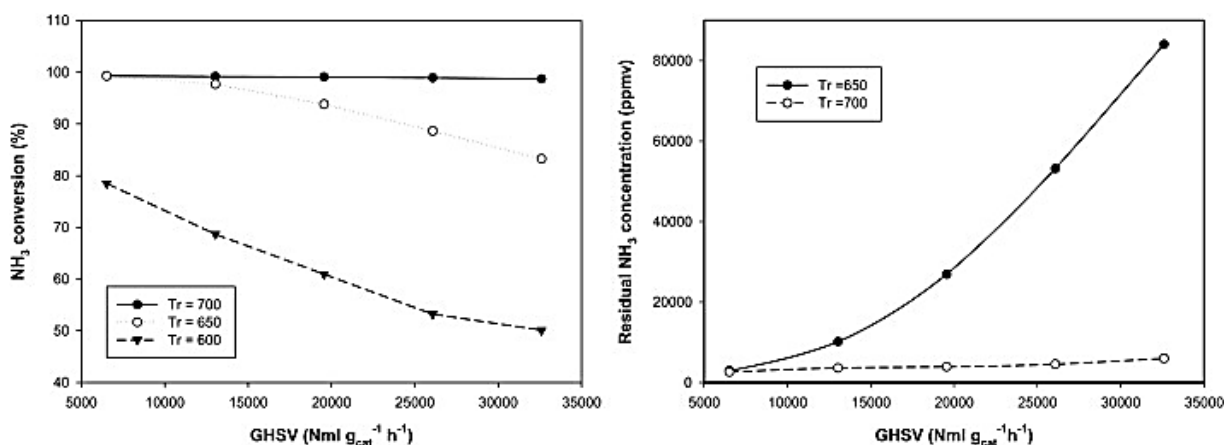


Fig. 3-6 Effect of space velocity (GHSV) on NH_3 conversion (left) and residual NH_3 concentration (right). Experimental conditions: $T_r = 600\text{--}700$ °C, atmospheric pressure

In Fig.3-6 (right), the residual NH_3 concentration in the produced reformat decreased with space velocity from 84 000 ppmv to 2 900 ppmv at 650 °C. At a glance, the results show no significant change in residual NH_3 concentration at 700 °C. On closer observation (Fig.3-7), it can be seen that residual NH_3 decreased from 6 000 ppmv to 2 600 ppmv for the range of space velocity considered. The approach to equilibrium residual NH_3 concentration is estimated to be 19.2% even at the lowest GHSV and highest reaction temperature. So, the NH_3 in the produced reformat must be reduced five-fold in order to at least attain the equilibrium value (500 ppmv).

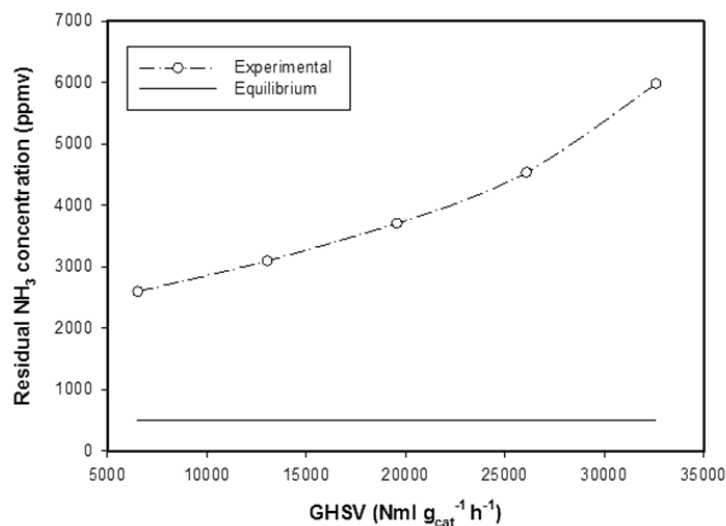


Fig. 3-7 Approach to residual NH_3 equilibrium concentration as a function of GHSV at $T_r = 700$ °C.

The NH_3 tolerance limit applicable to PEM fuel cells certainly appears elusive for all operating conditions considered in evaluating the microchannel reformer. Yet, operating the reformer at very-high-temperature (e.g. 900 °C) may be another forceful strategy that could further reduce the residual NH_3 in the reformat gas. But then again, very-high-temperatures impose momentous material and design challenges in consequence of H_2 embrittlement, high-temperature corrosion and ultimately complex fabrication of microchannels even if other high-temperature material substrates such as Alloy 617 are chosen for reactor construction. Besides,

at this very-high-temperature, the residual NH_3 at equilibrium conversion (150 ppmv) is still far greater than PEM fuel cell tolerance limit. A residual NH_3 clean-up unit is therefore mandatory prior to feeding the produced reformat to a PEM fuel cell.

3.3.4 Effect of reformer temperature and space velocity on H_2 production

Hydrogen production was also investigated over the same range of reaction temperature and GHSV as previous experiments. The results shown in Fig.3-8 show that at a definite temperature, H_2 production rate increased with increasing space velocity. Again, this trend was more observable at high reaction temperatures i.e. 650 °C and 700 °C. The microchannel reformer produced a maximum H_2 yield of $2.4 \text{ mol H}_2 \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ corresponding to $P_{\text{eq}} = 5.7 \text{ W}_e$ at $32\,600 \text{ Nml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and 700 °C. There was no difference in H_2 production for the reformer operating at 650–700 °C and space velocities below $19\,560 \text{ Nml g}_{\text{cat}}^{-1} \text{ h}^{-1}$. For these space velocities, 650 °C may be an attractive reformer temperature in view of possibilities of achieving similar power output at reduced thermal requirement and insulation volume. Overall, reformer operation at high temperature and space velocity tend to dictate faster H_2 production rates at the expense of higher NH_3 conversion. A system analysis involving trade-offs may be required to establish the optimal balance between these critical performance variables.

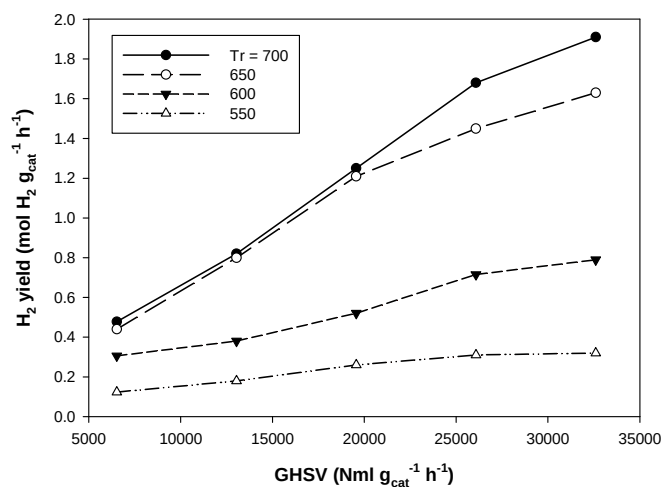


Fig. 3-8 H₂ yield as a function of space velocity and reactor temperature

3.3.5 Pressure drop analysis

In Fig.3-9, the pressure drop characteristics of the microchannel reformer are shown over various conditions of temperature and space velocity. The reformer demonstrated low pressure drop less than 1 kPa for all conditions. In fact, the reformer produced a maximum pressure drop of 740 Pa (10 Pa mm⁻¹) at the highest NH₃ flow rate (50 Nml min⁻¹) and highest reaction temperature (700 °C). Low pressure drop operation has operational advantages in view of increased system efficiency and reduced balance-of-plant. In this regard, the NH₃ cylinder pressure (8 bar) is sufficient to drive flow within the reformer and fuel cell system, neglecting the need for forced flow and associated components.

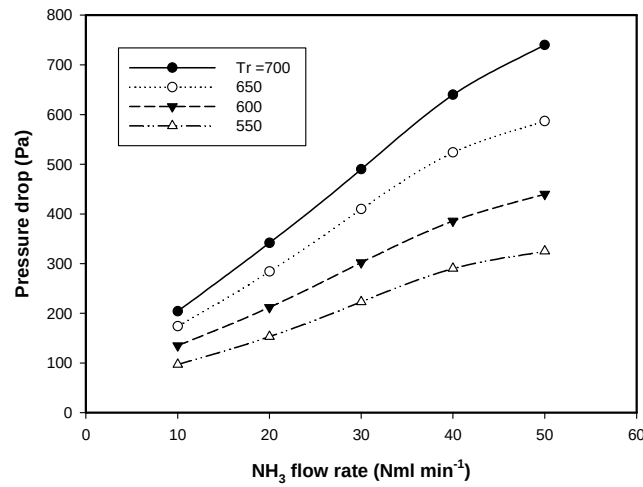


Fig. 3-9 Pressure drop as a function of reactor temperature and GHSV

3.3.6 Operational considerations for microchannel reformer

From the reported results, the operating conditions for best performance were chosen such that the reformer could produce H₂ with the lowest residual NH₃ in the reformat gas and at a sufficiently high throughput, all to attain a sizable power density. These were summarised in Table 3-2. The values indicated that the microchannel reformer can only be used with a clean-up device which may reduce the residual NH₃ in the reformat gas to the PEM fuel cell tolerance limit. The suitable adsorbents must be selected with robustness and longevity being the critical performance aspects to be evaluated. Otherwise, the reformat gas produced may only be directly fed to a fuel cell that is not susceptible to NH₃ poisoning. Incidentally, special deliberations based on reformer performance are required in selecting an appropriate combination of reformer and fuel cell technology. In one of their numerous communications, Kordes et al. [40] conclude that an AFC is not sensitive to relatively low NH₃ owing to the alkaline electrolyte that rejects caustic NH₃. Although it is still mandatory to obtain high NH₃ conversions, the residual NH₃ tolerance is less strict for an AFC thereby presenting an opportunity to operate the microchannel reformer either at lower reaction temperature or at higher space velocity. In addition, a low reformer energy efficiency of 14.1% (based on LHV)

was attained owing to the use of electric cartridge heaters in providing reaction heat for the endothermic NH_3 decomposition. An auto-thermal mode of operation achieved by thermal-coupling is most likely to increase the reformer efficiency.

Table 3-2 Summary of best performance of microchannel reformer

Feed	Pure NH_3
Catalyst	Ni-Pt/ γ - Al_2O_3
Reaction temperature ($^\circ\text{C}$)	700
Reactor pressure (bara)	0.88
GHSV ($\text{Nml g}_{\text{cat}}^{-1} \text{h}^{-1}$)	32 600
NH_3 conversion (%)	98.7
Residual NH_3 (ppmv)	6 000
H_2 production rate (Nml min^{-1})	67.5
Cold start-up time demand (min)	10
Power density ($\text{kW}_e \text{L}^{-1}$)	15.8 ^a
Reactor pressure drop (Pa mm^{-1})	10
Reactor efficiency (%)	14.1

^aEstimated based on effective reactor volume defined as volume through which the gas flows i.e. total channel and manifold volume.

3.3.7 Performance comparison with other ammonia reformers

The performance obtained by the microchannel reformer was compared with that attained by other micro-structured reactors reported in literature for H_2 generation via pure NH_3 decomposition. The various performance aspects were compared and results summarised in Table 3-3. It was however difficult to compare these microreactors owing to some important performance parameters not being reported in various works. For instance, pressure drop is only specified in [23] and this work. In addition, this paper is the only one to report the catalyst mass used in the reactor. Also, it is not clear whether the reactor volumes reported are overall or effective volumes; in our case we report both the overall volume (estimated using external dimensions of the reactor) and effective volume is given in brackets (Table 3-3). Most importantly, there are inconsistencies in determining P_{eq} . To circumvent this problem, we recalculated the power outputs based on the reported H_2 production rates and according to the

commonly-used Eq.4 in Section 2.4. The adjusted values are in parenthesis under the relevant column in Table 3-3.

Table 3-3 Comparison of global performance of microstructured reactors for pure NH₃ decomposition

Microreactor Configuration	Catalyst	Overall catalyst weight (mg)	Reactor volume (cm ³)	Reactor temperature (°C)	NH ₃ flow rate (Nml min ⁻¹)	NH ₃ conversion (%)	Power (W _e)	Power density (kW _e L ⁻¹)	Pressure drop (Pa mm ⁻¹)	Ref.
Channel	Ru/Al ₂ O ₃	-	1,000	600	-	>99.5	50 (-)	-	-	[21, 22]
Channel	Ir/Al ₂ O ₃	-	0.11	900	6	97	1.6 (0.7)	6.4	33.3	[23]
Post ^a	Ru/Al ₂ O ₃	-	0.3	650	50	63	13 (3.6)	12	-	[41]
Channel	Ru/Al ₂ O ₃	-	0.35	600	145	99	60 (17.4)	49.7	-	[24]
Packed-bed ^b	Ru	-	1.43	650	10	98	5.4 (1.2)	0.84	-	[42]
Channel	Ni-Pt/Al ₂ O ₃	92	18 (0.36)	700	50	98.7	5.7	0.32 (15.8)	10	This work

^aPost microreactor

^bPacked-bed microreactor

Our microchannel reformer performs relatively well against the other reactors. Apart from the reactor in [24] which achieved 99% NH₃ conversion at a higher flow, the reformer used in this study produced arguably the best conversion albeit at a slightly higher temperature. Interestingly, the Ni-Pt catalyst used in the reformer performs comparatively well against the more expensive Ru-based catalysts used elsewhere. In addition, the pressure drop and power output reported for the reformer in this work was also outstanding. The microchannel reformer however appears to be larger compared to other reactors resulting in a somewhat low power density (based on overall volume). This drawback can be solved by reducing channel number and length. Conversely, the power density based on effective volume is impressive. Overall, the microchannel reactor developed in this work demonstrated noteworthy H₂ production characteristics over a relatively wide operating space.

3.4 Conclusions

The stand-alone ammonia-fuelled microchannel reformer with washcoated commercial Ni-Pt catalyst was successfully operated for more than 900 h and showed pleasing stability. Its performance was investigated by varying the reaction temperature and space velocity, then

evaluating their effects on key performance variables vis-à-vis NH_3 conversion rate, residual NH_3 concentration, H_2 production rate, and pressure drop. The best performance was obtained at a reaction temperature of 700 °C and space velocity of 32 600 $\text{Nml g}_{\text{cat}}^{-1} \text{h}^{-1}$ where the reformer produced 98.7% NH_3 conversion and 67.5 $\text{Nml min}^{-1} \text{H}_2$ corresponding to a power density of 15.8 $\text{kW}_e \text{L}^{-1}$. Despite this impressive performance, a suitable clean-up unit subsequent to the microchannel reformer is certainly required for a reformat intended for a PEM fuel cell stack.

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CHAPTER 4: A MODELLING EVALUATION OF AN AMMONIA-FUELLED MICROCHANNEL REFORMER FOR HYDROGEN GENERATION

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Abstract

Hydrogen production from an ammonia-fuelled microchannel reactor is simulated in a three-dimensional (3D) model implemented via Comsol Multiphysics™. The work described in this paper endeavors to obtain a mathematical framework that provides an understanding of reaction-coupled transport phenomena within the microchannel reactor. The transport processes and reactor performance are elucidated in terms of velocity, temperature, and species concentration distributions, as well as local reaction rate and NH₃ conversion profiles. The baseline case is first investigated to comprehend the behavior of the microchannel reactor, then microstructural design and operating parameters are methodically altered around the baseline conditions to explore the optimum values. The simulation results show that an optimum NH₃ space velocity (GHSV) of 65.2 NI g_{cat}⁻¹ h⁻¹ yields 99.1% NH₃ conversion and a power density of 32 kW_e L⁻¹ at the highest operating temperature of 973 K. It is also shown that a 40-μm-thick porous washcoat is most desirable at these optimum conditions. Finally, a low channel hydraulic diameter (225 μm) is observed to contribute to high NH₃ conversion. Mass transport limitations in the porous-washcoat and gas-phase are negligible as depicted by the Damköhler and Fourier numbers, respectively. The experimental microchannel reactor yields 98.2% NH₃ conversion and a power density of 30.8 kW_e L⁻¹ when tested at the optimum operating conditions established by the model. Good agreement with experimental data is observed, so the integrated experimental-modeling approach developed in this paper may well provide an incisive step toward the efficient design of ammonia-fuelled microchannel reformers.

Keywords: ammonia decomposition, microchannel reactor, hydrogen generation, modelling evaluation, computational fluid dynamics, reaction-coupled transport phenomena

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Chapter 4: A modelling evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation

Nomenclature			
a_i	stoichiometric coefficient of species i	$\langle V \rangle$	fluid velocity in porous region (m s^{-1})
C_F	Forchheimer drag coefficient	v_i	atomic diffusion volume of species i ($\text{cm}^3 \text{mol}^{-1}$)
C_{H_2}	local H_2 concentration (mol m^{-3})	v_j	atomic diffusion volume of species j ($\text{cm}^3 \text{mol}^{-1}$)
C_{in}	concentration of NH_3 at inlet (mol m^{-3})	v_x, v_y, v_z	velocity components in x, y, z directions (m s^{-1})
C_{pi}	specific heat capacity of species i ($\text{J kg}^{-1} \text{K}^{-1}$)	W	channel width (μm)
$C_{p,eff}$	effective specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)	X_{NH_3}	NH_3 conversion (%)
C_{ps}	specific heat capacity of catalyst ($\text{J kg}^{-1} \text{K}^{-1}$)	y_i	mole fraction of species i
C_{NH_3}	local NH_3 concentration (mol m^{-3})	Greek symbols	
D	species diffusivity ($\text{m}^2 \text{s}^{-1}$)	α	channel aspect ratio
D_H	channel hydraulic diameter (μm)	δ_s	porous washcoat thickness (μm)
D_{ij}	binary diffusivity of species i in j ($\text{m}^2 \text{s}^{-1}$)	ε	porosity
$D_{ij,eff}$	effective binary diffusivity ($\text{m}^2 \text{s}^{-1}$)	Λ	mean free path (nm)
Da	Darcy number	μ_B	Brinkmann viscosity (Pa s)
Dam	Damköhler number	ρ	density of fluid (kg m^{-3})
E_a	activation energy (J mol^{-1})	ρ_s	density of catalyst (kg m^{-3})
F_{in}	molar flux at inlet (mol s^{-1})	κ	permeability (m^2)
F_{out}	molar flux at outlet (mol s^{-1})	ω_i	mass fraction of species i
Fo	Fourier number	$\langle \omega \rangle$	mass fraction of species i in porous region
H	channel height (μm)	τ	residence time (s)
ΔH_r	reaction enthalpy (J mol^{-1})	τ_d	internal diffusion timescale (s)
k	thermal conductivity of fluid ($\text{W m}^{-1} \text{K}^{-1}$)	τ_D	external diffusion timescale (s)
k_{eff}	effective thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)	τ_r	reaction timescale (s)
k_o	pre-exponential factor ($\text{mol g}^{-1} \text{h}^{-1} \text{bar}^{-1}$)	μ	viscosity of fluid (Pa s)
k_s	thermal conductivity of catalyst ($\text{W m}^{-1} \text{K}^{-1}$)	Subscripts and superscripts	
Kn	Knudsen number	a	activation
L	channel length (m)	atm	atmosphere
M_i	molecular weight of species i (kg mol^{-1})	cat	catalyst
M_j	molecular weight of species j (kg mol^{-1})	$cnst$	constant
$\mathbf{n}$	normal unit vector	eff	effective
P	pressure (Pa)	in	inlet
P_{atm}	atmospheric pressure (atm)	out	outlet
$\langle P \rangle$	pressure in porous domain (Pa)	r	reaction
R	reaction rate ($\text{mol m}^{-3} \text{s}^{-1}$)	s	catalyst
R_{cnst}	ideal gas constant ($82.057 \text{ cm}^3 \text{atm K}^{-1} \text{mol}^{-1}$)	w	wall
R_r	reaction rate ($\text{mol kg}^{-1} \text{s}^{-1}$)	Abbreviations	
Re	Reynolds number	CFD	computational fluid dynamics
Re_k	pore Reynolds number	FSG	Fuller-Schettler-Giddings
T	temperature (K)	$PARDISO$	parallel sparse direct linear solver
T_w	wall temperature (K)	PEM	polymer electrolyte membrane
$\langle T \rangle$	temperature in porous region (K)	$ppbv$	parts per billion volume
u_{in}	fluid velocity at inlet (m s^{-1})		

4.1 Introduction

PEM fuel cells using hydrogen (H_2) fuel are expected to be used extensively as alternative power sources in various portable and distributed applications. The low volumetric energy density of H_2 however makes difficult its transportation and storage to isolated locations. This present lack of an adequate H_2 delivery infrastructure presents one of the few important challenges to the widespread implementation and commercialization of PEM fuel cell systems in distributed applications. Consequently, the on-site generation of H_2 via reforming of alternative H_2 carriers in fuel processors is considered a promising stop-gap solution [1,2]. In view of this, the processing of several H_2 carriers has been proposed in literature. Among these, ammonia decomposition (also commonly referred to as ammonia reforming) has lately been receiving increased attention for various desirable reasons.

Table 4-1 Specific and volumetric energy densities of common fuels and power sources [3]

Fuel	H_2 content (wt %)	Gravimetric energy density (Wh/kg)	Volumetric energy density (Wh/L)
Ammonia	17.7	4 318	4 325
Methanol	12.5	6 400	4 600
Methanol (incl. water*)	-	2 040	-
Ethanol	13	7 850	6 100
Ethanol (incl. water*)	-	2 578	-
Hydrogen (700 bar)	100	39 000	1 305
Gasoline	15.8	12 200	9 700
Gasoline (incl. water*)	-	2 140	-
Li-polymer battery	-	110	300

* Including mass of water for steam reforming

Most importantly, NH_3 is a CO_x -free H_2 carrier that has superior H_2 content and gravimetric energy density compared to other alternative carriers (Table 4-1) [3–5]. In addition, NH_3 is an inexpensive fuel (US\$₂₀₁₃580 ton^{-1} [6]) that has an extensive and well-developed manufacturing-distribution infrastructure worldwide to guarantee uninterrupted fuel supply. Also, the availability of NH_3 is incontestable given that the annual global NH_3 production capacity continues to grow by more than 20% [7]. Unlike steam reforming of hydrocarbon fuels, NH_3

decomposition is a simple one-step process that has inherent cost benefits in view of reduced mass management challenges and balance-of-plant [3]. Economic analyses have however revealed that ammonia decomposition is more attractive than natural gas and methanol reforming only for small-to-medium scale ($<100 \text{ Nm}^3 \text{ h}^{-1}$) hydrogen generation [8–10]. One of the near-term small scale applications having great value proposition is the replacement of diesel generators to supply on-site power at off-grid telecommunication towers. At present, approximately 640,000 diesel-generator-powered off-grid telecom installations exist in the world and these are growing at 12% per annum primarily due to the emergence of developing economies [3, 11].

Notwithstanding, conventional fixed-bed reactors for ammonia decomposition have size and weight characteristics that can barely serve the needs of a compact fuel cell system [12]. Microchannel reactors have been identified as a transformative technology for realizing ammonia-fuelled reformers for portable and distributed H_2 generation [3]. This reactor technology enables on the one hand to reduce substantially the size footprint of the overall system and on the other hand enhance the heat and mass transfer rates [13–16]. Yet, optimal operation of microchannel reactors remains elusive due to the difficulty in obtaining real-time parameter profile data within the microstructure. Even traditional measurement techniques interfere and alter the local flow field within the microchannels, rendering impractical the attainment of accurate real-time data [17–19].

In spite of the remarkable microchannel reformer performance obtained in a previous experimental study by the authors [20], reaction-coupled transport phenomena occurring inside the microchannels are not sufficiently understood to explain the achieved performance. Similarly, Deshmukh et al. [21] note that experimental results do not easily extend to the design and optimization of the microchannel reactor. A different approach is therefore desirable for obtaining absolute clarity of flow, heat, and mass transfer phenomena within the experimental

microchannel reactor. Chiuta et al. [3] mentioned the usefulness of a combined experimental-mathematical approach to attain accurately optimized microchannel designs. Most importantly, a mathematical model can genuinely provide important information on transport conditions at any point within the microchannel without disturbing the flow dynamics.

Literature is lacking in reporting mathematical modelling of microchannel reactors for NH_3 decomposition [3]. Although few two-dimensional (2-D) models exist for spatially-coupled microchannel reactors [22–25], no model has been presented hitherto for a stand-alone microchannel reactor. The importance of obtaining an optimized stand-alone reactor design before considering the complex issues of thermal coupling is emphasized in reports [20] and [26]. The work reported in this paper builds on and uses the experimental results observed in [20] to validate the mathematical model. In any case, the literature base on integrated experimental-mathematical characterization of microchannel reactors for NH_3 decomposition is extremely sparse. Arana et al. [27] executed an experimental study for a microchannel reactor combined with 2-D heat transfer modelling, the latter serving to elucidate the heat-loss mechanisms and not the heat transport within the microstructure.

This work purports to investigate fundamental transport phenomena and design and operating parameter effects on the global performance of a stand-alone ammonia-fuelled microchannel reactor. Specifically, a mathematical framework for understanding the relevant interactions between various physical and chemical processes is developed. For this purpose, a three-dimensional (3-D) multi-physics model that comprises continuity, momentum, mass and energy equations adapted to appropriate microchannel reactor domains (free-fluid and catalytic porous washcoat) is developed. An important open question is whether the microstructural geometry and operating conditions for the experimental reactor reported in [20] are optimal? The overall aim is to derive guidelines for the design and practical implementation of microchannel reactors for NH_3 decomposition.

4.2 Mathematical model development

In summary, the development of the mathematical model for the ammonia-fuelled microchannel reactor involves correctly identifying the computational geometry and establishing appropriate governing equations and boundary conditions for the respective computational domains. Most importantly, the model and kinetic parameters are specified *a priori*. Finally, a suitable solution method is obtained to simultaneously solve for the governing equations. These aspects of model development are illustrated in detail in Sections 2.1 to 2.6.

4.2.1 Model geometry

The simulated geometry consists of a single rectangular microchannel ($H = 150\ \mu\text{m}$, $W = 450\ \mu\text{m}$, $L = 50\ \text{mm}$), which is assumed to behave the same as the other channels constituting the microchannel reactor (constructed in collaboration with the Institut für Mikrotechnik Mainz, Germany). This single-channel modelling approach assumes equal partitioning of the fluid by the intake distribution manifold, and is a common concept accepted in literature [28–30]. The microchannel computational geometry basically consists of an open gap (free-fluid region) along which the reactants flow, and a porous catalytic washcoat layer ($\delta_s = 40\ \mu\text{m}$) adjacent to the flow gap. The catalyst washcoat is deposited on three of the four channel walls, and heat flux to these walls is supplied via electric heaters [20]. Owing to the symmetry of the channel, a half-width channel is considered for the simulation.

4.2.2 Model assumptions

The mathematical behaviour of the partial differential equations for continuity, momentum, mass and energy depends on the following specified assumptions;

- a) The flow is steady and laminar.
- b) The gas mixture behaves as an ideal gas.
- c) The gas flow is taken as weakly compressible to take account of the slight density variations due to temperature and volumetric/composition changes.

- d) The washcoated catalyst is treated as an isotropic porous media.
- e) The porous washcoat and gas mixture are at local thermal equilibrium.
- f) Homogeneous reactions are ignored.

The physics occurring within the microchannel dictate the use of a 3-D mathematical model. Specifically, reactants and product species diffuse to and from the wall-coated catalyst layers, while bulk flow occurs in the axial direction. Velocity, temperature, and concentration variations therefore have to be accounted for in the axial and transverse directions.

4.2.3 Governing equations

Based on the above assumptions, the governing equations used in formulating the mathematical model are given in Table 4-2. The Knudsen number ($Kn = \lambda / D_H$) for the characteristic reactor dimensions used in this study are of the order 10^{-4} . This is less than the critical value of 10^{-3} [31], hence the continuum theory and Navier-Stokes equations are valid for describing momentum conservation in the free-fluid domain. The fluid density is computed from the ideal gas law for a multicomponent mixture. For the coupled free fluid-porous problem considered here, the Darcy number ($Da = \kappa / \delta^2$) is greater than 10^{-4} [32], hence non-Darcian flow exists in the porous washcoat. The Brinkman-Forchheimer-extended Darcy equations are therefore used to describe momentum conservation for flow in the coupled porous washcoat domain. For details see [33, 34], and associated references. The pore Reynolds number ($Re_k = \rho v \sqrt{k} / \mu$) is evaluated and found to be smaller than 1, so that the contributions of convective and non-linear Forchheimer inertia (turbulent drag) terms in the generalized Brinkman-Forchheimer-extended Darcy equations are ignored. The drag force due to fluid flow in the porous media (viscous force) remains the only source term in the Brinkmann equations.

To determine the temperature profiles, one energy equation is considered for the porous washcoat based on the assumption of local thermal equilibrium [35]. This includes a heat source (consumption) term due to the endothermic NH_3 decomposition. The Stefan-Maxwell

multicomponent diffusion model along with convective mass transfer is used to describe species conservation within the free-fluid and porous washcoat. This model will not be described in more detail here, but the reader is referred elsewhere [36, 37] for an extensive theoretical treatment. The source term representing the net species generation or consumption only applies to the porous washcoat where chemical reactions occur.

Table 4-2 Mathematical model governing equations used for simulating microchannel behaviour

Free fluid phase:
<i>Continuity equation</i>
$\nabla \cdot (\rho \mathbf{V}) = 0$
<i>Navier-Stokes equations</i>
$\mathbf{V} \cdot \nabla (\rho \mathbf{V}) = -\nabla P + \nabla \cdot (\mu \nabla \mathbf{V})$
<i>Energy equation</i>
$\nabla \cdot (\rho C_p \mathbf{V} T) = \nabla \cdot (k \nabla T)$
<i>Species continuity equation</i>
$\nabla \cdot (\rho \omega_i \mathbf{V}) = \nabla \cdot (\rho D_{ij} \nabla \omega_i)$
<i>Ideal gas law</i>
$\rho = \frac{P}{R_{\text{const}} T} \sum_{i=1}^3 y_i M_i$
Catalyst washcoat phase:
<i>Continuity equation</i>
$\nabla \cdot (\varepsilon \rho \mathbf{V}) = 0$
<i>Brinkman-Forchheimer-extended Darcy Equations</i>
$\mathbf{V} \cdot \nabla (\varepsilon \rho \mathbf{V}) = -\nabla P + \nabla \cdot \left(\frac{\mu_B}{\varepsilon} \nabla \mathbf{V} \right) - \frac{\mu}{\kappa} \mathbf{V} - \frac{\rho \varepsilon C_F}{\kappa} \mathbf{V} \mathbf{V}$
<i>Energy equation</i>
$\nabla \cdot (\varepsilon \rho C_p \mathbf{V} T) = \nabla \cdot (k_{\text{eff}} \nabla T) + (1 - \varepsilon) \Delta H_r \rho_s R_r$
<i>Species continuity equation</i>
$\nabla \cdot (\varepsilon \rho \omega_i \mathbf{V}) = \nabla \cdot (\varepsilon \rho D_{ij, \text{eff}} \nabla \omega_i) + (1 - \varepsilon) \sum_{i=1}^3 \alpha_i M_i \rho_s R_r$

4.2.3.1 Transport and physical properties

The generally used hypothesis of constant thermo-physical properties cannot be used in accurately modelling microchannel reactors [38, 39]. Therefore, temperature-dependent

properties (viscosity, thermal conductivity, and heat capacity) of individual gas species used here are obtained from the Korean Thermo-physical Properties Data Bank [40] and ChemCAD™ properties database. These are subsequently used to evaluate the corresponding gas mixture properties as a function of local composition using the mass-fraction weighted mixing law. For example;

$$C_p = \sum_{i=1}^3 \omega_i C_{pi} \quad (1)$$

The effective properties of the porous media are all expressed in the same form as;

$$k_{eff} = \varepsilon k + (1 - \varepsilon)k_s \quad (2)$$

The binary diffusion coefficients are estimated based on the Fuller-Schettler-Giddings (FSG) equation (Eq. 3). Reid et al. [41] evaluated the different binary diffusivity estimation methods and recommend the FSG equation based on the smallest error.

$$D_{ij} = \frac{0.000143 T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}}}{P_{atm} \left[\sum v_i^{\frac{1}{3}} + \sum v_j^{\frac{1}{3}} \right]^2} \quad (3)$$

The effective diffusion coefficients appearing in the species conservation equations for the porous catalyst layer are calculated using the Bruggeman correlation (Eq. 4), which accounts for the effect of porous matrix on gas phase mass transport [42].

$$D_{ij,eff} = D_{ij} \varepsilon^{1.5} \quad (4)$$

The thermal conductivity and specific heat capacity of the porous washcoat are estimated using the most widely used Neumann-Kopp rule [43]. Values of porosity and permeability of the washcoat are assumed following an extensive analysis of literature, where porosity values

range from 0.4–0.6 and permeability values range from 10^{-8} – 10^{-12} m². However, sensitivity of the model to variations in microstructural effects is performed over the entire range.

Table 4-3 Initial and boundary conditions for mathematical model

Channel inlet	
$v_x = v_x^{in}$ $v_y^{in} = v_z^{in} = 0$ $T^{in} = T_w$ $\omega_{NH_3}^{in} = 1$	
Channel outlet	
$P = 0$ $\frac{\partial T}{\partial x} = \frac{\partial v}{\partial x} = \frac{\partial \omega_i}{\partial x} = 0$	
Channel walls	
$v_x = v_y = v_z = 0$ $T = T_w$ $\frac{\partial \omega_i}{\partial n} = 0$	
Symmetry	
$\frac{\partial v_x}{\partial n} = \frac{\partial v_y}{\partial n} = \frac{\partial v_z}{\partial n} = \frac{\partial T}{\partial n} = \frac{\partial \omega_i}{\partial n} = 0$	
Interface	
$\mathbf{V} = \langle \mathbf{V} \rangle$ $P = \langle P \rangle$ $T = \langle T \rangle$ $\omega_i = \langle \omega_i \rangle$	

4.2.4 Boundary conditions

The governing equations are solved subject to the boundary and initial conditions specified in Table 4-3. At the inlet, pure ammonia flows into the channel with a uniform velocity equal to the average velocity. Tonkovich et al. [44] mention that reactants in a microchannel reactor flow-by and not through the catalyst. And so, the cross-sectional area corresponding to the open gap is used to calculate the average inlet velocity. Ammonia feed to the reactor is assumed to heat up quickly within the intake distribution manifold so that the feed temperature at the inlet is equal to the wall temperature (reactor temperature). In fact, initial modelling results show the predicted pressure drop to be within range of the experimental values if inlet temperature assumes the value of the wall temperature. At the exit, atmospheric pressure is imposed for the momentum conservation equations, and normal gradients (with respect to direction of flow) are set to zero for velocity, temperature and species mass fraction. The reactor substrate is held at constant temperature and the channel walls are therefore modelled by imposing a constant temperature (H1) boundary condition at the catalyst-wall interface.

The no-slip boundary condition is applied at each wall-fluid interface. Also, symmetry boundary conditions are imposed at the plane of symmetry i.e. a zero normal gradient is applied to all dependent variables to signify no flow across the plane of symmetry. At the free-fluid porous catalyst interface; continuity in velocity, pressure, temperature, and species fluxes is imposed. This continuity is implicitly taken into account within the Brinkmann-Forchheimer-extended Darcy model [33]. Work detailing the caveats and effects of different interface treatments is further discussed in [33] and [34].

4.2.5 Chemical reaction kinetics

The source term for the species continuity equations in the porous catalyst domain requires explicit specification of the reaction kinetics data. Chellappa et al. [45] showed that first-order power law kinetics (Eq. 5) with respect to ammonia (Tamaru model) sufficiently predicted the ammonia conversion to within 5% of experimental values. The hydrogen inhibition phenomenon described by the Temkin-Pyzhev kinetics simply does not occur at the temperature range investigated in this work. In their study, k_0 and E_a values were found to be 1.309×10^{12} (mol g⁻¹ h⁻¹ bar⁻¹) and 2.05×10^5 (J mol⁻¹), respectively. The experimental reactor used in our earlier reported work [20] contained the same commercial Ni-Pt/Al₂O₃ catalyst so that the rate law of Chellappa et al.[45] is applied in the present work.

$$R_r = k_0 \exp\left(\frac{-E_a}{RT}\right) P_{NH_3} \quad (5)$$

4.2.6 Solution method

The governing equations are discretized and solved numerically using the finite element-based COMSOL Multiphysics™ simulation software (Comsol, Inc., version 4.3a). An adaptive mesh (Fig 4-1) is used and the priority is to increase prediction accuracy in important regions. For instance, the computational mesh close to the free-fluid-porous media interface and near-wall regions is extremely refined to capture the sharp velocity, temperature, and species concentration gradients. All simulations were performed on a 2.90 GHz Intel processor with 4

GB RAM. The direct solver (PARDISO) with parametric sweep is used where the convergence criterion for each variable is restricted to a relative tolerance of 10^{-3} .

Table 4-4 Evaluating mesh independency

Maximum centreline velocities for various mesh grids at different wall temperatures							
Mesh elements	T_w (K)						Solution time (h)
	723	773	823	873	923	973	
44 000	0.445	0.452	0.496	0.649	0.847	0.897	13
64 240	0.455	0.455	0.500	0.659	0.855	0.899	42
94 200	0.456	0.461	0.510	0.673	0.870	0.913	226

To examine the mesh-independence of the solution, 3 mesh grids with different number of mesh elements are considered. The influence of the different mesh grids on the prediction of local velocity distributions for a typical case is presented in Table 4-4. The maximum deviation for the solutions is less than 3%, which is an acceptable error. 44 000 free-triangular mesh elements are therefore chosen to discretize the entire geometry, whilst achieving a trade-off between accuracy and CPU time.

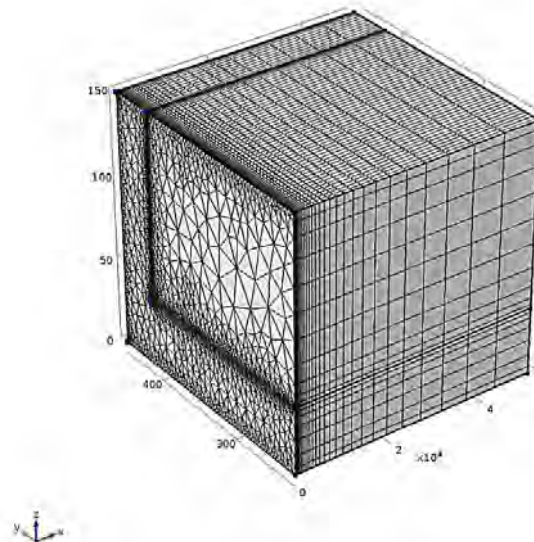


Fig. 4-1 Discretized microchannel geometry used in CFD simulations

Table 4-5 Base-case simulation conditions

Geometrical conditions	
Microchannel length, L (m)	0.05
Microchannel width, W (μm)	450
Microchannel height, H (μm)	150
Porous washcoat thickness (μm)	40
Washcoat material	
Porosity, ϵ	0.4
Permeability, κ (m^2)	1×10^{-12}
Thermal conductivity, k_s ($\text{W m}^{-1} \text{K}^{-1}$)	32
Specific heat capacity, $C_{p,s}$ ($\text{J kg}^{-1} \text{K}^{-1}$)	860
Catalyst density, ρ_s (kg m^{-3})	770
Inlet conditions	
Composition, ω (%)	100% NH_3
Velocity, u_{in} (m s^{-1})	0.25
Temperature, T (K)	973

4.3. Results and discussion

4.3.1 Model validation

The CFD model results are directly validated against the corresponding experimental results reported in [20], and a detailed comparison of experiment vs. model is shown in Fig.4-2. Six simulations are performed where NH_3 conversion is investigated as a function of reactor temperature (Fig 4-2a). It is observed that NH_3 conversion is favoured by high reactor temperatures. NH_3 conversion is calculated according to Eq. 6;

$$X_{\text{NH}_3} = \frac{F_{in} - F_{out}}{F_{in}} \quad (6)$$

In addition, the model is validated against pressure drop data for the high reactor temperatures (923–973 K) as shown in Fig.4-2(b). It is also important to verify the accuracy of the model at conditions which correspond to low NH_3 conversion. In view of this, the model validity is examined as a function of NH_3 flow rates (10–50 Nml min^{-1}) at low to intermediate reactor temperatures (Fig 4-2c). Overall, CFD simulation results agree well with the experimental data

and the model can be used with confidence, to investigate further the fundamental transport phenomena occurring within the microchannel reactor.

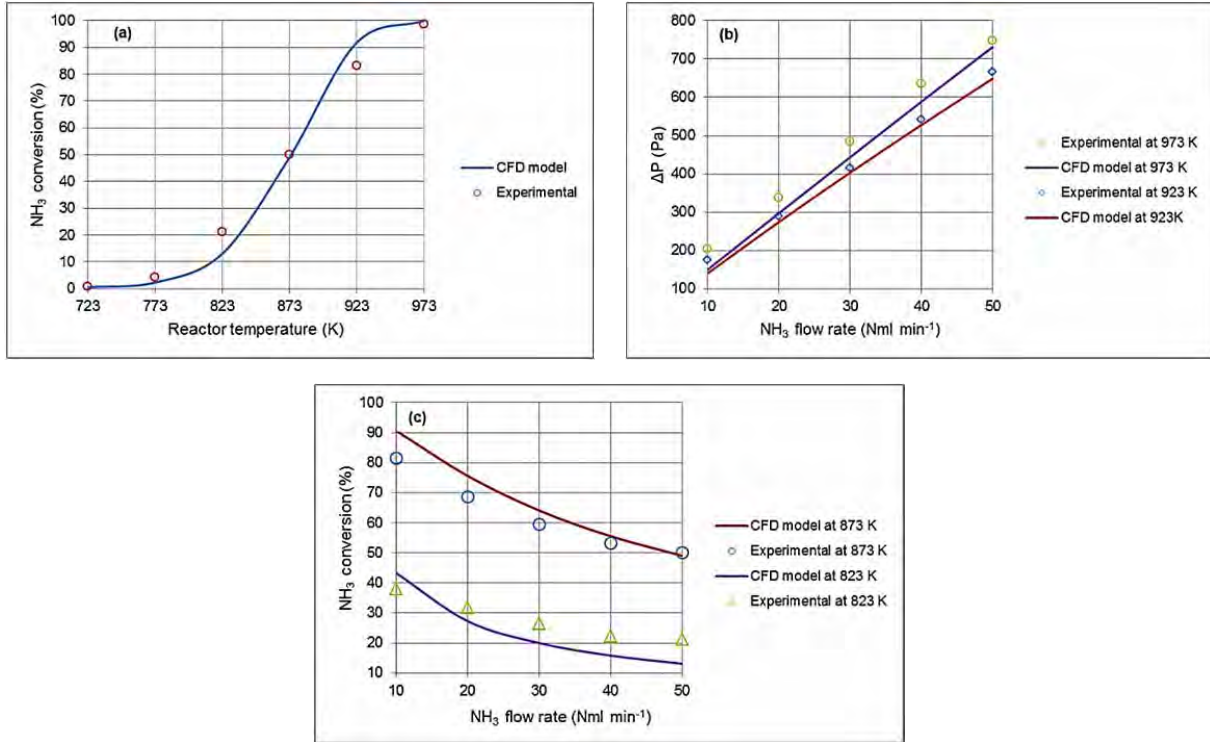


Fig. 4-2 Comparison of CFD simulation results with experimental data: (a) NH₃ conversion as a function of reactor temperature at base case simulation conditions (Table. 4-5). (b) Pressure drop as a function of NH₃ flow rate at high reactor temperatures (923–973 K). (c) NH₃ conversion as a function of NH₃ flow rate at low and intermediate reactor temperatures (823–873 K).

4.3.2 Velocity, temperature, and concentration distributions

This section presents the basic features of the velocity, temperature, and concentration profiles within the microchannel for the baseline simulation conditions stipulated in Table 4-5. At these conditions, the experimental microchannel reactor exhibited the best performance, and in the present work, they represent a reference standard upon which the influence of various parameters is evaluated. In Fig 4-3(a), a fully-developed velocity profile resembling laminar flow in a duct is clearly seen in the free-fluid region at axial position $x = 2.5$ cm. For the base case simulation conditions, the flow field is observed to develop to a full profile at axial position $x = 2$ cm. The axial centreline velocity is shown to increase to a maximum of 0.9 m s^{-1} . However, the average velocity at the channel outlet (0.49 m s^{-1}) is approximately twice the magnitude of the

inlet velocity. This is attributed mainly to gas expansion caused by a net species generation (of factor 2) via the NH_3 decomposition reaction. The transverse velocity components (v_y and v_z) were established to be too small ($<10^{-4} \text{ m s}^{-1}$) to have a significant effect on the flow field.

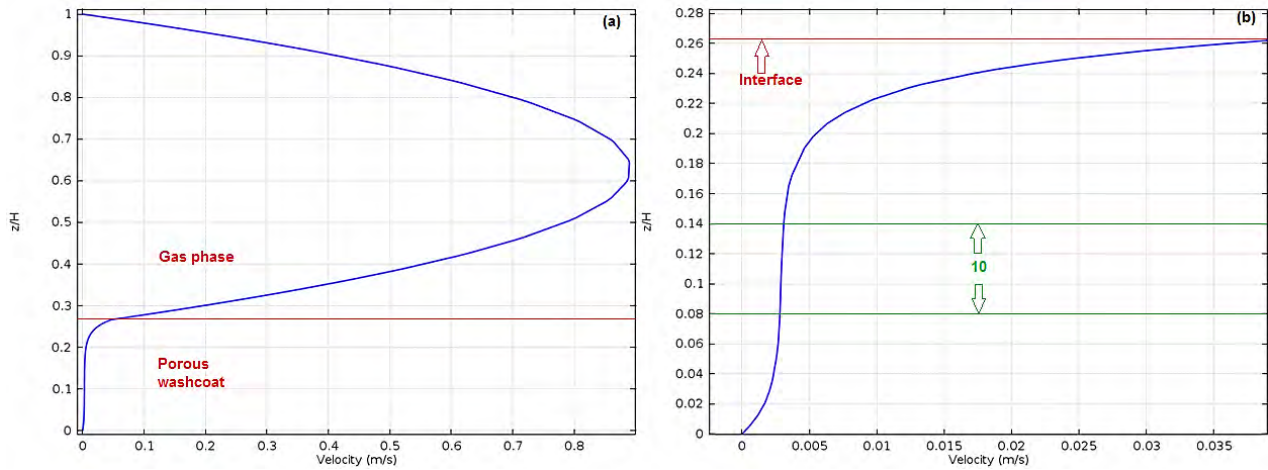


Fig. 4-3 (a) Axial velocity distribution in the transverse direction (normalized channel height, z/H) at axial location $x = 2.5 \text{ cm}$ (b) Zoomed view of the axial velocity profile within the porous washcoat in the transverse direction at axial location $x = 2.5 \text{ cm}$. Reaction conditions are given in Table 4-5.

A free-slip transition in velocity is evident at the porous-fluid interface. The retarded flow in the region close to the interface is evidence of momentum transport by viscous effects, which Darcy's law does not take into account. Fig 4-3(b) shows clearly the existence of velocity gradients within the porous washcoat also suggesting significant viscous momentum transfer into the porous media. The velocity in the porous washcoat is small (of the order 0.003 m s^{-1}) except in the region close to the interface. Also, the velocity profile within the porous washcoat across $0.08 < z/H < 0.14$ is fairly flat, indicating ideal plug flow ensues within this 10- μm - thick region.

The effect of permeability on the velocity profiles in the gas phase and porous washcoat is investigated and results are shown in Fig 4-4. It is observed that a larger permeability allows more NH_3 gas permeation (higher convective flow in porous region), resulting in a reduced maximum centreline (axial) velocity in the free-fluid. The change in NH_3 conversion subsequent to alterations in axial velocity profiles is however insignificant (0.4%). Most literature considers

permeability values for porous washcoat within this range, and the obtained result is conclusive in pointing out that permeability is of little importance in the design of ammonia-fuelled microchannel reformers.

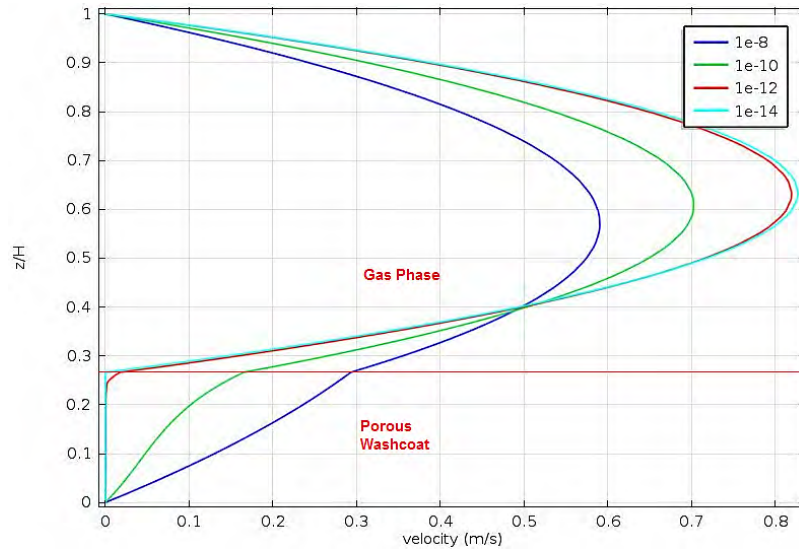


Fig. 4-4 Effect of permeability on gas phase and porous washcoat velocity distributions. Operating conditions are specified in Table 4-5.

In Fig. 4-5(a–b), the temperature profile development within the microchannel is shown. The temperature drop near the entrance is attributed to the heat sink produced by the mildly endothermic NH_3 decomposition reaction. The temperature gradient is however sufficiently small (0.04 K) that the microchannel reactor operates under isothermal conditions, and at the same time dominates the endothermic effects. This ability to render excellent heat transfer is one of the benefits associated with the microchannel reactor. It is observed from Fig 4-5(b) that the reactor length required to achieve a fully-developed temperature profile is longer for higher NH_3 flow conditions.

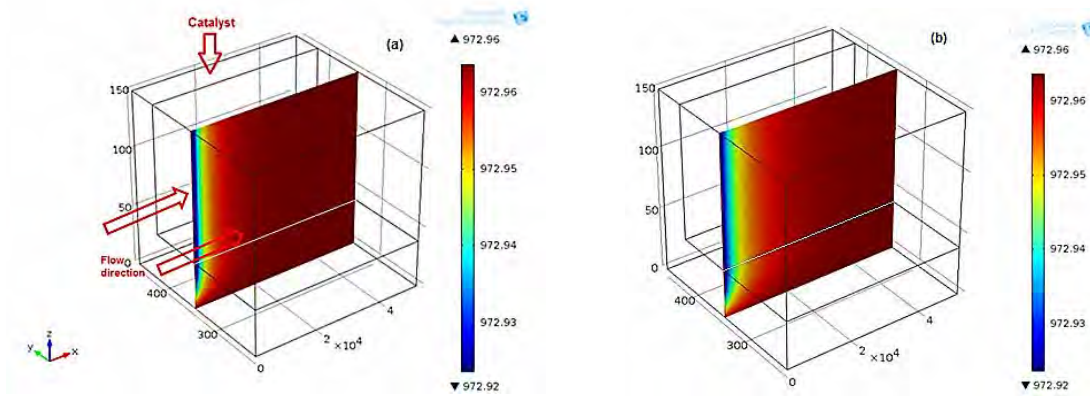


Fig. 4-5 Contours of temperature in the mid x-z plane along the microchannel length for (a) baseline simulation conditions ($T = 973\text{ K}$, NH_3 flow rate $= 50\text{ Nml min}^{-1}$) (b) optimal conditions ($T = 973\text{ K}$, NH_3 flow rate $= 100\text{ Nml min}^{-1}$).

Fig.4-6 (a–b) show the NH_3 and H_2 concentration profiles in both the fluid and porous regions at four axial positions; $x = 10\text{--}60\text{ }\mu\text{m}$. The concentration gradients dictate that NH_3 diffuses into the porous washcoat whilst H_2 diffuses out of the porous region into the bulk phase. An analysis of the species concentration gradients at different axial locations in the transverse direction (Fig 4-6) shows that the NH_3 decomposition reaction occurs to a large extent within the porous washcoat at the entrance region. Specifically, a sharp concentration gradient is shown for $x = 10\text{ }\mu\text{m}$. In addition, the large transverse concentration gradients (for $x < 30\text{ }\mu\text{m}$) show that the reaction is particularly strong in the interface region and up to a depth of $25\text{ }\mu\text{m}$ into the porous washcoat. It is observed that there exist small concentration gradients even towards the substrate wall, indicating that the entire catalyst thickness of $40\text{ }\mu\text{m}$ is fully utilized. However, the small magnitude of these near-wall concentration gradients could be an indication that porous washcoat thicknesses $>40\text{ }\mu\text{m}$ may not be useful. On the other hand, the concentration gradients within the open channel (gas phase) are negligible.

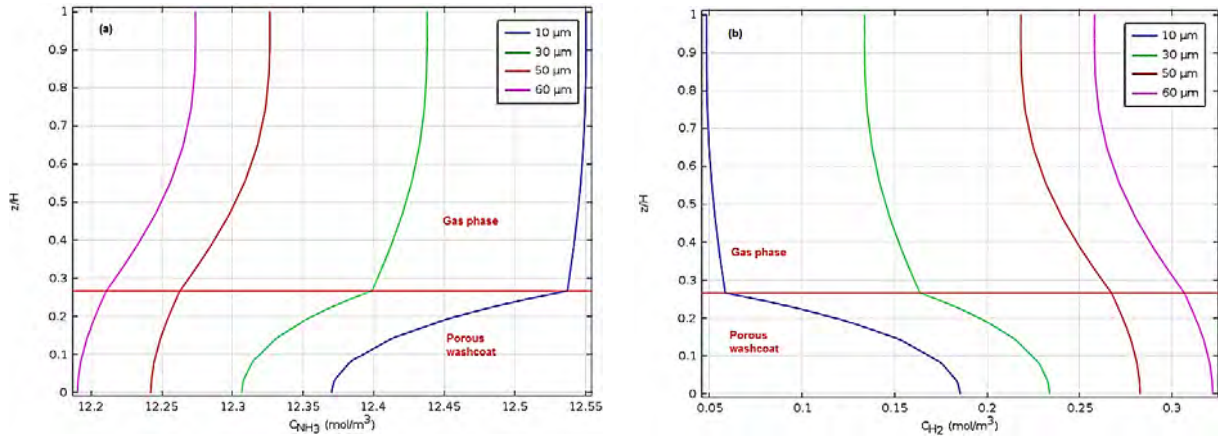


Fig. 4-6 (a) NH_3 concentration distribution in the transverse direction (normalized channel height, z/H) at axial locations $x = 10, 30, 50$, and $60 \mu\text{m}$ from microchannel inlet (b) H_2 concentration distribution in the transverse direction at axial location $x = 10, 30, 50$, and $60 \mu\text{m}$ from microchannel inlet. Reaction conditions are given in Table 4-5.

Species mole fractions and local reaction rate along the microchannel length are presented in Fig.4-7. Clearly, NH_3 concentration decreases whilst H_2 concentration increases along the length of the reactor. It is observed that 80% of the NH_3 decomposes within 10% of the microchannel length due to high reaction rate at the highest temperature (Fig 4-7b). This result also confirms the qualitative analysis drawn from Fig 4-6 that the reaction is strongest at the entrance. For the baseline conditions, the reaction is practically complete within 60% of the reactor length. The practical significance is that the reactor length can be reduced to 3 cm to obtain the same performance. This leads to a reduced reactor volume, which effectively enhances the power density of the reformer. Otherwise, it is indispensable to examine conditions for which the entire reactor length is fully utilized. The details of the required optimization are given in Section 3.3.

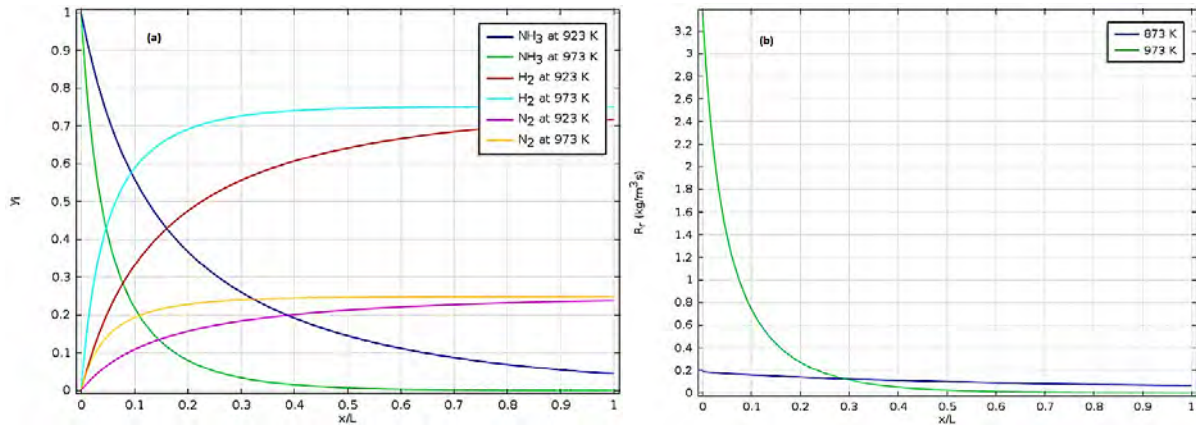


Fig. 4-7 (a) Species mole fraction distribution along reactor length for baseline simulation conditions (b) Variation of local reaction rate with temperature along reactor length.

4.3.3 Best design and operating conditions

The best conditions are defined as design and operating conditions at which the reactor attains >99% NH_3 conversion (<1% residual NH_3 in reformat) and at the same time produces satisfactory power density (hydrogen yield) whilst maintaining a low pressure drop. We envisage this target provides a trade-off that establishes balance between faster H_2 productivity and low residual NH_3 in the reformat gas. It is also important to note that best conditions are defined for a maximum operating temperature of 973 K seeing that very-high-temperatures are much likely to impose momentous material and design challenges such as high-temperature corrosion and H_2 embrittlement [20]. For what concerns best reactor operation, design/operating conditions are explored by varying the NH_3 flow rate, catalyst layer thickness, and channel hydraulic diameter.

4.3.3.1 Effect of NH_3 flow rate

In Fig. 4-8(a), it is observed that the entire catalyst length is fully utilized when the NH_3 flow rate is higher than that at baseline conditions (50 Nml min^{-1} , corresponding to $\text{Re} = 3.5$ in the channel), inferring that the reaction region expands down the reactor length due to higher fluid velocity. The optimum flow rate is chosen to attain the NH_3 conversion achieved at baseline simulation conditions (99.5%). Evidently, Fig.4-8(a) shows that 99.1% NH_3 conversion is attained at $\text{Re} = 7$ (corresponding to an NH_3 flow of 100 Nml min^{-1} through the reactor). The

practical implication of this result is that the reactor can be operated at double the flow rate (100 Nml min^{-1}), to attain almost the same NH_3 conversion. This represents an excellent operating target for the ammonia-fuelled microchannel reactor (Fig 4-8b).

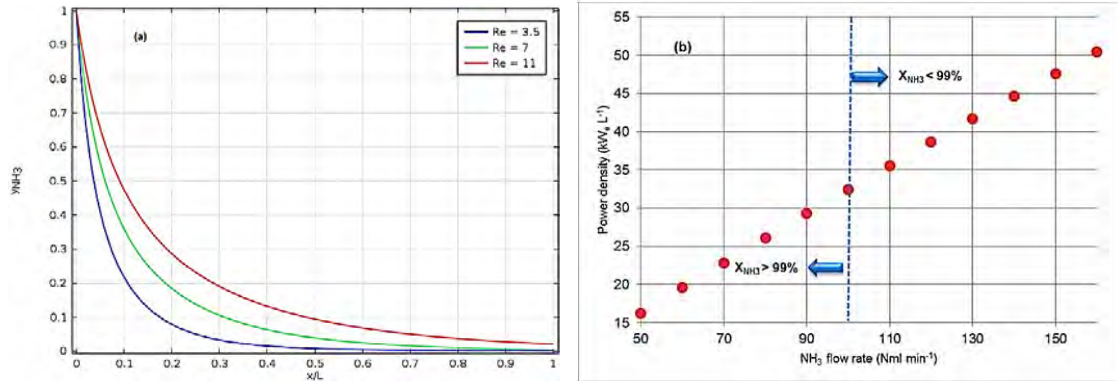


Fig. 4-8 Effect of NH_3 flow rate on (a) reactor length utilization and (b) power density. Curves for $Re = 3.5$, $Re = 7$, and $Re = 11$ correspond to the baseline (50 Nml min^{-1}), optimal (100 Nml min^{-1}), and maximum-flow (160 Nml min^{-1}) cases, respectively.

It is noteworthy the PEM fuel cells tolerance of 100 ppbv residual NH_3 in reformat gas is beyond equilibrium, and remains unattainable even for very high temperatures [20]. Consequently, the reformat gas will need a clean-up unit prior to feeding a PEM fuel cell stack. Although the clean-up unit will be slightly larger, the benefits of operating the reactor at an NH_3 flow of 100 Nml min^{-1} far outweigh the drawbacks in that hydrogen productivity and power density increase (Fig 4-8b). In fact, the CFD model predicts that the experimental microchannel reformer can attain twice the power density established in [20], apart from an insignificant (0.4%) decrease in NH_3 conversion. The operation of the microreactor at much higher NH_3 flow ($>100 \text{ Nml min}^{-1}$) results in reduced NH_3 conversion, but H_2 productivity and power density are however enhanced (Fig 4-8b). In addition, high flow operation is preferable for high-power devices and applications which require fast response to frequent power fluctuations.

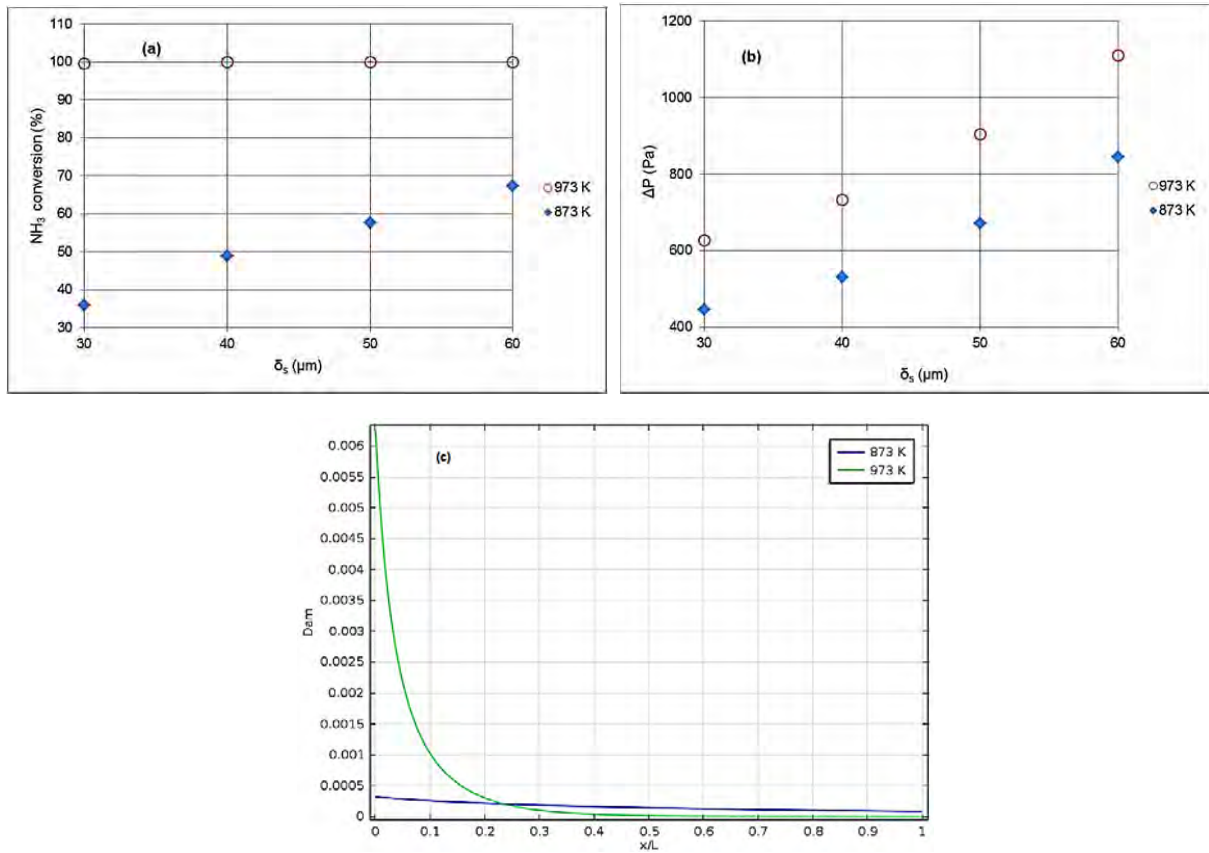


Fig. 4-9 Effect of porous washcoat thickness on (a) NH₃ conversion (b) Pressure drop. (c) Axial profiles of Damköhler number for a 50- μm -thick porous washcoat.

4.3.3.2 Effect of catalytic porous washcoat thickness

The influence of the porous washcoat thickness on reactor performance is simulated for the highest and intermediate operating temperatures. The washcoat thickness is varied up to 90 μm in the simulation, but only results for a practical thickness range (<60 μm) are shown in Fig.4-9. The simulations are performed at a constant space velocity (taken from the base case) to ascertain that any change in reactor performance is precisely due to variation in washcoat thickness, otherwise, the result can be attributed to a combination of varying flow rate and washcoat thickness.

The results in Fig 4-9(a) show that NH₃ conversion at 973 K is practically the same (99.66–99.99%) for the corresponding washcoat thickness range (30–60 μm). This result can be understood in the context of equilibrium-limited operation rather than internal mass transfer

resistance. The reactor operation at 973 K is so close to equilibrium that a change in washcoat thickness has an indistinguishable effect on NH_3 conversion. Fig 4-9(c) shows the axial profiles of the local Damkohler number [46], from which there is evidence showing that NH_3 decomposition is reaction-controlled ($Dam < 0.1$). For higher flow operation however, there is possible significant momentum transfer (flow field) into the porous washcoat, and internal diffusion limitations must be explored further. The local Damköhler number (Dam) is defined as a ratio of local diffusion to reaction timescales in the porous washcoat (Eq. 7).

$$Dam = \frac{\tau_d}{\tau_r} = \frac{R\delta_s^2}{D_{eff}C_{in}} \quad (7)$$

For the most part, pressure drop is shown (Fig 4-9b) to increase for no change in NH_3 conversion at 973K. Overall, washcoat thicknesses $>40 \mu\text{m}$ can barely be considered useful at the highest operating temperature. This conclusion is consistent with the observation drawn from a qualitative analysis of the concentration gradients in Fig 4-6.

For 873 K, operation is still far from thermodynamic equilibrium and the effect of varying the porous washcoat thickness is clearly elucidated in Fig 4-9 (a). A thicker washcoat helps to secure a higher NH_3 conversion, at the expense of increasing pressure drop. The enhancement in performance is largely due to the thicker catalyst having more active sites to convert the NH_3 . Fundamentally, the increase in conversion with washcoat thickness also demonstrates the absence of intraphase mass transfer resistance. This further confirms the Damköhler number analysis in Fig 4-9(c).

4.3.3.3 Effect of channel size

The influence of channel size on reactor performance is evaluated against channel hydraulic diameter (D_H). In this simulation, D_H is changed using various channel aspect ratios (α) as shown in Table 4-6. Similar to Section 3.3.2, the simulations are performed at a constant space velocity (taken from the base case: Case 2) to ascertain that any change in reactor

performance is precisely due to variation in D_H . The results show that the general trend is for NH_3 conversion to decrease with increasing D_H . This can be clearly seen at the intermediate temperature (873 K), which represents an operating condition far removed from equilibrium.

Table 4-6 Effect of channel size on reactor performance and external mass transfer

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
α	0.25	0.33	0.5	1	2	4
H (μm)	150	150	250	300	600	600
W (μm)	600	450	500	300	300	150
D_H (μm)	240	225	333	300	400	240
X_{NH_3} (%) at 973 K	99.8	99.9	99.4	99.7	99.6	99.9
X_{NH_3} (%) at 873 K	43.2	48.9	34.2	42.7	36.9	68.2
Fo at 973 K	6 759	7 692	3 512	4 327	2 434	6 759
Fo at 873 K	5 591	6 360	2 904	3 578	2 013	5 591

These results could be interpreted from the point of view that diffusional (molecular) distance of reactants to the porous washcoat increases with D_H (e.g. Case 2 vs. Case 5). For the case in point, the diffusional resistance evaluated via the Fourier (Fo) number [47, 48] in (Eq.8–9) is at least three-times less for the smaller channel (Case 2) as compared to Case 5. Despite a slightly larger D_H , Case 6 is observed to have the best performance, superseding that of Case 2. However, the channel volume for Case 6 is 25% greater than that for Case 2, and at 973 K, a microchannel reactor with channel dimensions of Case 2 will have a greater power density.

$$Fo = \frac{\tau}{\tau_D} \quad (8)$$

$$\tau_D = \frac{D_H^2}{4D} \quad (9)$$

For what concerns the external mass transfer limitations, computations of Fo number (Table 4-6) for the respective channels show that the diffusion time scale is very low compared

to residence time. This suggests that the NH_3 molecules have enough time to reach the porous washcoat before they exit the reactor. Most importantly, Fo is greatest for Case 2, which demonstrates transverse mass transfer is more efficient for the smaller channels. In summary, external mass transfer limitations are of no importance for the conditions and channel gap sizes considered.

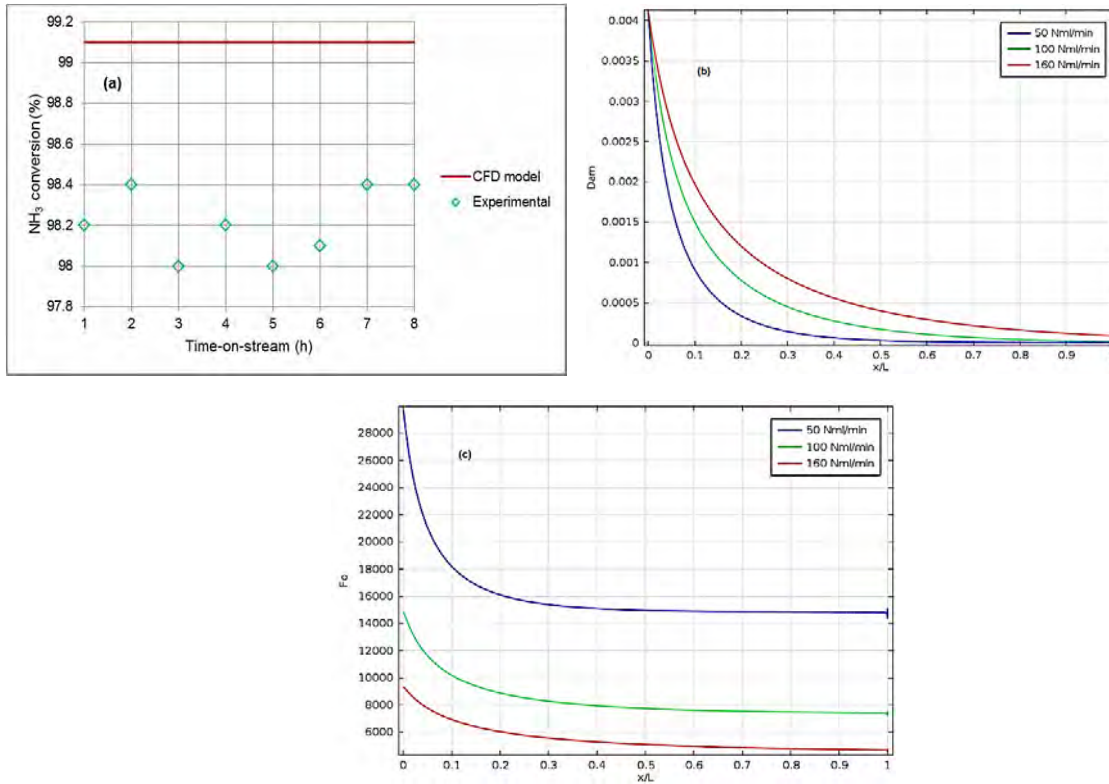


Fig. 4-10 (a) Experiment vs. CFD model results for NH_3 conversion as a function of time-on-stream for the optimum conditions (b) Axial profiles for Damköhler number as a function of NH_3 flow rate for the optimum microchannel geometry (c) Axial profiles for Fourier number as a function of NH_3 flow rate for the optimum microchannel geometry.

4.3.4 Experimental performance evaluation at predicted best conditions

In order to further substantiate the model results, the performance of the microchannel reactor is experimentally investigated at the best conditions predicted by the model. The comparison shown in Fig.4-10(a) depicts that there is good agreement between the experimental and modelling result for NH_3 conversion (98.2% vs. 99.1%), as well as for power density ($32.4 \text{ kW}_e \text{ L}^{-1}$ vs. $30.8 \text{ kW}_e \text{ L}^{-1}$). In addition, internal and external diffusion limitations are investigated further at the different NH_3 flow rates (space velocities) as shown in Fig.4-10 (b–c).

Although Fo decreases with increasing space velocity (decreasing τ), it is still much higher than the critical value and so external mass transport limitations are not important even at these high flow rates. Similarly, the reaction rate is much slower for higher flow rates and so the Dam falls off to an asymptote at a slower rate. Still, $Dam \ll 0.1$, so that internal diffusion limitations in the washcoat are not important for all flow conditions considered.

4.4 Conclusions

In this work, a three-dimensional model has been developed to provide an understanding and prediction of the transport phenomena and physico-chemical interactions within a stand-alone ammonia-fuelled microchannel reactor. The mathematical model does not only simulate the fluid flow, but also considers heat transfer and reaction aspects within the flow (multi-physics model). Fluid flow, heat and mass transfer were modelled by appropriate governing equations in the gas phase and porous washcoat and by realistic boundary conditions (no lumped heat and mass transfer coefficients were used). The velocity, temperature, concentration, and reaction rate profiles as well as microchannel geometry effects have been studied. The following main conclusions are drawn from the work described in this paper:

- 1) High NH_3 conversions and H_2 productivity are obtained under high-temperature operation.
- 2) Temperature gradient along the microchannel reactor length is small so that operation is effectually isothermal.
- 3) Increase in porous washcoat thickness generally increases NH_3 conversion, but at a penalty of increased pressure drop. A thickness above $40\mu\text{m}$ is deemed useless.
- 4) Efficient mass transfer for channels with smaller hydraulic diameter is noted resulting in better NH_3 conversion.

- 5) For all conditions considered, the NH_3 decomposition is strongly reaction-controlled ($Da_m < 0.1$) and external mass transfer resistance is so small ($Fo > 1$) to influence reaction rate.
- 6) The optimal design parameters of the microchannel reactor are as follows: $L = 5$ cm; $D_H = 225$ μm ; 40- μm -thick porous washcoat. The experimental microchannel reactor considered in [20] therefore has the optimal microstructural configuration. However, the following operation strategy must be used to yield optimal performance: $T = 973$ K, $GHSV = 65.2$ $\text{NL g}_{\text{cat}}^{-1} \text{h}^{-1}$; all to yield a fuel cell equivalent power density of $30.8 \text{ kW}_e \text{ L}^{-1}$.
- 7) The model exceptionally captures the performance of the experimental reactor and can certainly be used as a design tool for different (microstructural) configurations of microchannel reactors for H_2 generation via NH_3 decomposition.

Acknowledgements

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CHAPTER 5: PERFORMANCE EVALUATION OF A HIGH-THROUGHPUT MICROCHANNEL REACTOR FOR AMMONIA DECOMPOSITION OVER A COMMERCIAL Ru-BASED CATALYST

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Abstract

In this work, the prospect of producing hydrogen (H_2) via ammonia (NH_3) decomposition was evaluated in an experimental stand-alone microchannel reactor wash-coated with a commercial Ruthenium-based catalyst. The reactor performance was investigated under atmospheric pressure as a function of reaction temperature (723–873 K) and gas-hourly-space-velocity (65.2–326.1 $NI\ g_{cat}^{-1}\ h^{-1}$). Ammonia conversion of 99.8% was demonstrated at 326.1 $NI\ g_{cat}^{-1}\ h^{-1}$ and 873 K. The H_2 produced at this operating condition was sufficient to yield an estimated fuel cell power output of 60 W_e and power density of 164 $kW_e\ L^{-1}$. Overall, the microchannel reactor considered here outperformed other NH_3 microstructured reformers reported in literature including the Ni-based system used in previous work by these authors. Furthermore, the microchannel reactor showed a superior performance against a fixed-bed tubular microreactor with the same Ru-based catalyst.

Keywords: ammonia decomposition, microchannel reactor, ruthenium catalyst, hydrogen generation, fuel cells, performance evaluation

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Chapter 5: Performance evaluation of a high-throughput microchannel reactor for ammonia decomposition over a commercial Ru-based catalyst

Nomenclature			
H_c	channel height (μm)	GC	gas chromatograph
L_c	channel length (mm)	GHSV	gas-hourly-space-velocity ($\text{NI g}_{\text{cat}}^{-1} \text{h}^{-1}$)
m_{cat}	mass of catalyst in reactor (mg)	HID	helium ionization detector
$\dot{m}_{\text{H}_2}$	mass flow rate of hydrogen (kg s^{-1})	LHV	low heating value (kJ kg^{-1})
$\dot{m}_{\text{NH}_3, \text{out}}$	mass flow rate of residual ammonia (kg s^{-1})	PEM	polymer electrolyte membrane
$\dot{m}_{\text{NH}_3, \text{in}}$	mass flow rate of ammonia at inlet (kg s^{-1})	ppbv	parts per billion volume
$n_{T, \text{in}}$	total molar flow rate at reactor inlet (mol s^{-1})	ppmv	parts per million volume
$n_{T, \text{out}}$	total molar flow rate at reactor outlet (mol s^{-1})	TCD	thermal conductivity detector
P	pressure (Pa)		
P_{eq}	fuel cell power output equivalent (W_e)		
Q_e	cartridge heater power requirement (kJ s^{-1})		
Q_{H_2}	molar hydrogen production rate (mol h^{-1})		
R	ideal gas constant ($82.057 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$)		
T	temperature (K)		
T_r	reactor operating temperature (K)		
v_{H_2}	volumetric hydrogen production rate at outlet ($\text{cm}^3 \text{ h}^{-1}$)		
W_c	channel width (μm)		
W_f	fin width (μm)		
X_{NH_3}	ammonia conversion (%)		
$y_{\text{NH}_3, \text{in}}$	ammonia mole fraction at reactor inlet		
$y_{\text{NH}_3, \text{out}}$	residual ammonia mole fraction at reactor outlet		
Y_{H_2}	specific hydrogen production rate ($\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$)		
Greek symbols			
η	reformer energy efficiency (%)		
η_{PEM}	PEM fuel cell energy efficiency (%)		
Θ_{PEM}	PEM fuel cell hydrogen utilization (%)		
Sub-or superscripts			
c	channel		
cat	catalyst		
e	electric		
eq	equivalent		
f	fin		
in	inlet		
out	outlet		
r	reactor		
T	total		
Abbreviations			
AFC	alkaline fuel cell		
DSS	daily start-up and shut-down		

5.1 Introduction

The low volumetric energy density of H_2 fuel escalates the wide gap in the H_2 supply chain to deploy fuel cell technology at a large scale. Hardman and Steinberger-Wilckens [1] allude that successful infrastructural pre-development is essential in attaining a viable H_2 economy. On the foregoing, the existing lack of an adequate infrastructure provokes the need for on-site generation of H_2 via reforming of alternative H_2 carriers in fuel processors [2]. Among the various options, ammonia (NH_3) decomposition has lately been receiving increasing attention for various desirable reasons [3–7]. Most importantly, NH_3 is a carbon-free H_2 carrier that has superior H_2 content and gravimetric energy density compared to alternative carriers. Microchannel reactors are a transformative technology for realizing ammonia-fuelled reformers for portable and distributed H_2 generation. This reactor technology enables on the one hand to reduce substantially the size footprint of the overall system and on the other hand enhance the heat and mass transfer rates [5–10].

Very little work is however reported in literature on experimental investigation of microchannel fuel processors for NH_3 decomposition. The past decade has seen literature reporting only five experimental studies using microchannel reactors [5]. The details of these respective studies are furnished in our earlier communications [5, 6]. Lately, Chiuta et al. [6] evaluated, characterized, and demonstrated miniaturized H_2 production in an ammonia-fuelled microchannel reactor washcoated with a Ni-based catalyst. Their reformer yielded exceptional performance only for low ammonia flows ($<50 \text{ Nml min}^{-1}$), producing an estimated fuel cell power density of $15.8 \text{ kW}_e \text{ L}^{-1}$. The present paper seeks to evaluate a Ru-based microchannel reactor for pure NH_3 decomposition, and compare its global performance against that attained in our previous work [6] using a Ni-based catalyst. In this assessment, the improvement in performance vis-à-vis the Ru-based catalyst is articulated.

5.2 Experimental

5.2.1 Microchannel reactor design

The microchannel reactor (Fig.5-1) used for this work was designed and constructed in collaboration with Fraunhofer-ICT-IMM (Mainz, Germany). The reactor geometry was designed identical to that used in our previous study [6]. The microchannels were fabricated on a SS314 stainless steel (German steel classification 1.4841) plate having a thickness of 2 mm. The plate consisted of 80 microchannels ($H_c = 150 \mu\text{m}$, $W_c = 450 \mu\text{m}$, $W_f = 250 \mu\text{m}$, and $L_c = 50 \text{ mm}$), along with right-angled triangular header and footer manifolds at the inlet and outlet ends of the channels, respectively.

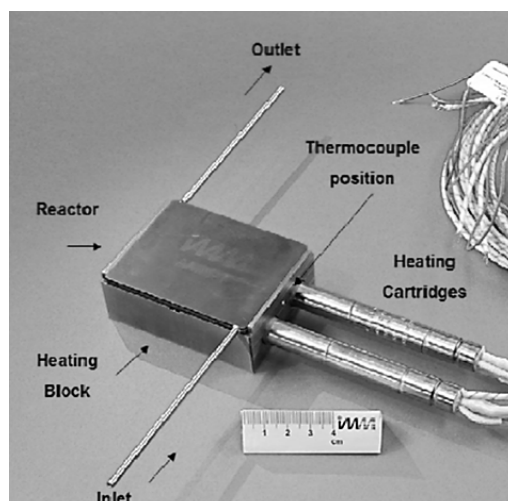


Fig. 5-1 Depictions of the reactor with laser-welded inlet/outlet tubes, heating block and electric heater cartridges

5.2.2 Catalyst preparation

A commercial Cesium-promoted 8.5 wt% Ru/Al₂O₃ (Hypermec 10010 [11]; BET surface area of 113 m² g⁻¹ and pore volume of 0.30 cm³ g⁻¹) catalyst supplied by ACTA S.p.A (Crespina, Italy) was used. The catalyst was deposited onto the microchannels using a sequential washcoating, drying and calcination procedure described elsewhere [12]. A catalyst washcoat layer thickness of 40 μm was achieved for each microchannel. The microchannel reactor plate carried a total 92 mg of catalyst, similar to that of the Ni loading in [6].

5.2.3 Experimental apparatus and procedure

5.2.3.1 Description of experimental reactor system

The experimental system similar to that used in our earlier work [6] is adopted for the present study. A Brooks SLA5850 thermal mass flow controller regulates pure NH_3 (Afrox, 99.99% min.) flow into the microchannel reactor. Likewise, H_2 (Afrox, 99.99% min.), and Ar used in the pretreatment of catalyst are regulated by respective Brooks SLA5850 thermal mass flow controllers. The heating to the microchannel reactor is achieved using two electric cartridge heaters regulated by a temperature controller. The reactor temperature is measured by two K-type thermocouples inserted at opposite ends (axial) into reactor housing. Pressure drop across the microchannel reactor is measured by an AT9000 DP pressure transmitter (Model GTX31D) capable of Pa-range accuracy. The flow rate of the reformat gas is measured by a soap-bubble meter. An online SRI8610C GC equipped with two TCDs, one HID, two Molecular Sieve 13X columns (1.8 m and 0.9 m), and one HayeSep D column (1.8 m) is used for analysis of the reformat gas composition downstream of the reactor.

5.2.3.2 Description of experimental procedure

Prior to the experiments, the catalyst was reduced at 823 K under flowing H_2 (50 Nml min^{-1}) for 2 h [10]. At the end of the pre-treatment, the system was adjusted to the desired reaction temperature under Ar flow (75 Nml min^{-1}) for 0.5 h to remove adsorbed H_2 . Reactor operating conditions including reaction temperature and GHSV were varied at atmospheric pressure. Four reaction temperatures between 723–873 K and in increments of 50 K were investigated. Ammonia feed flow rates between 100 and 500 Nml min^{-1} corresponding to 65.2–326.1 $\text{NI g}_{\text{cat}}^{-1} \text{h}^{-1}$ GHSV were used. The reactor operated in a daily start-up and shut-down (DSS)-like mode to mimic frequent intermittent operation envisaged for fuel cell systems [6]. In this mode, the reactor was started up in the morning then operating for 6 h before shut-down. Also, experiments were conducted one parameter at a time while keeping others constant. The reaction temperatures used in this study were not high enough (<1 273 K) to cause sufficient

catalytic acceleration of NH_3 decomposition by the Ni metal in the SS314 reactor substrate. In addition, the reactor walls were covered with catalyst layer, hence direct contact of the substrate with NH_3 reactant was limited. This is in agreement with the CFD modelling results published in an earlier communication [7] by these authors. For these reasons, blank studies for baseline decomposition were not done.

5.2.4 Reformer performance parameters

The important performance parameters used were NH_3 conversion, residual NH_3 concentration, H_2 yield, fuel cell power output equivalent, and pressure drop. Raw data from the experiments were used to calculate performance metrics, which are defined by Eq. 2–4:

$$X_{\text{NH}_3} = \frac{n_{T,in} y_{\text{NH}_3,in} - n_{T,out} y_{\text{NH}_3,out}}{n_{T,in} y_{\text{NH}_3,in}} \times 100\% \quad (2)$$

$$Y_{\text{H}_2} = \frac{\dot{Q}_{\text{H}_2}}{m_{cat}} = \frac{P \dot{v}_{\text{H}_2}}{RT m_{cat}} \quad (3)$$

$$P_{eq} = \eta_{PEM} \theta_{PEM} \dot{Q}_{\text{H}_2} LHV_{\text{H}_2} \quad (4)$$

The product of the last two terms in Eq.4 represents the thermal wattage of H_2 produced [2]. In addition, the energy efficiency (η) of the reformer was defined in Eq.5 as the lower combustion enthalpy rate of the product stream divided by the sum of the lower combustion enthalpy rate of the feed stream and the electric energy provided by cartridge heaters [13]. The microchannel reactor was well-insulated and heat loss to the surroundings was considered negligible.

$$\eta = \frac{(LHV_{\text{H}_2} \times \dot{m}_{\text{H}_2}) + (LHV_{\text{NH}_3} \times \dot{m}_{\text{NH}_3,out})}{(LHV_{\text{NH}_3} \times \dot{m}_{\text{NH}_3,in}) + Q_e} \quad (5)$$

5.3 Results and Discussion

5.3.1 Performance stability of microchannel reformer

A performance durability and stability test was conducted on the reformer over a 150-h continuous operation. This was done at the end of the experimental schedule after the reformer had endured approximately 400 h of DSS-like operation. The residual NH_3 in the reformat gas was monitored against time-on-stream and at conditions corresponding to the highest reaction temperature and space velocity (873 K and $326.1\text{ NI g}_{\text{cat}}^{-1}\text{ h}^{-1}$). The residual NH_3 concentration varied between $1\,020$ – $1\,100$ ppmv throughout the entire 150-h period (Fig. 5-2). These values are close to residual NH_3 concentration at equilibrium showing that the reformer was operated in a demanding region at these operating conditions. The results also revealed that frequent start-up and shut-down operation did not significantly affect the performance of the reformer.

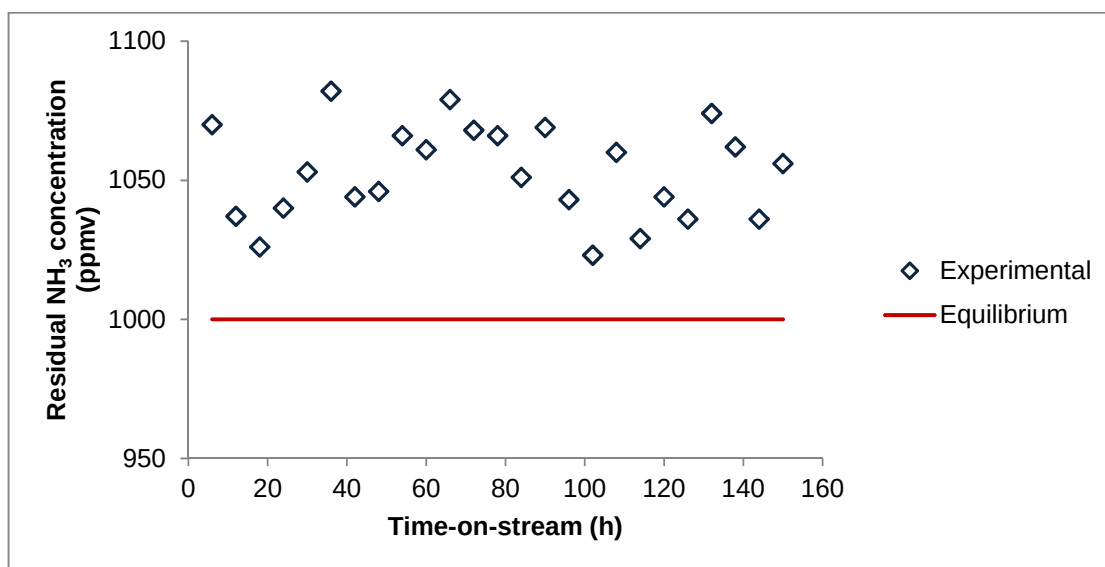
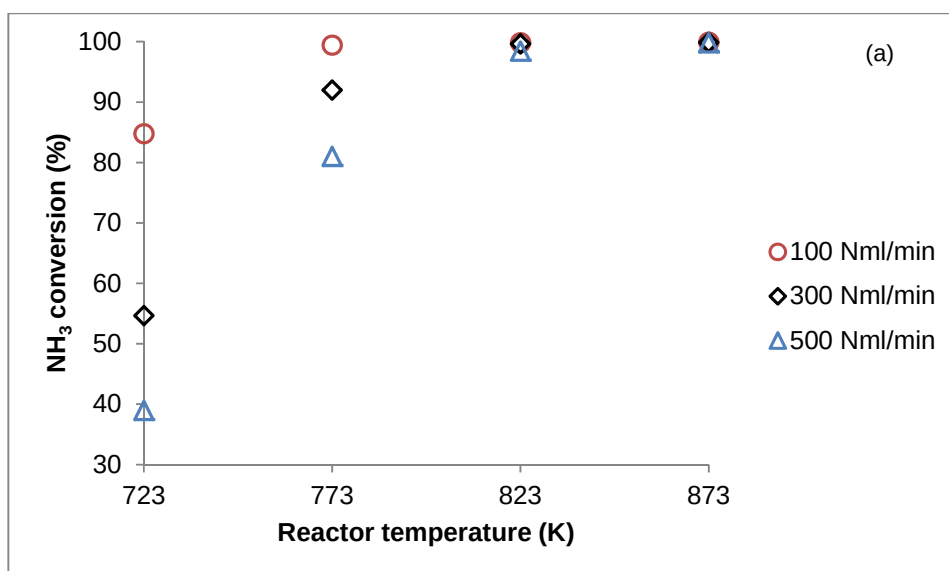


Fig. 5-2 Performance durability of microchannel reformer in NH_3 decomposition over Hypermec 10010® catalyst; residual NH_3 in reformat as a function of time-on-stream. Experimental conditions: $T_r = 873\text{ K}$, NH_3 flow rate = 500 Nml min^{-1} ($\text{GHSV} = 326.1\text{ NI g}_{\text{cat}}^{-1}\text{ h}^{-1}$). Residual NH_3 at chemical equilibrium is calculated at the specified reaction temperature and atmospheric pressure.

5.3.2 Effect of reformer temperature and space velocity on ammonia decomposition

The influence of reaction temperature on NH_3 conversion was explored at the lowest, intermediate, and highest NH_3 flow rates as shown in Fig. 5-3(a). Generally, NH_3 conversion

increased sharply with increase in reaction temperature and inclined to flatten off for $T_r > 823$ K. In contrast to the Ni-based system in [6], high NH_3 conversions were observed at low reaction temperatures. For instance, at 723 K and 100 Nml min^{-1} , NH_3 conversions of 85% and <2% were attained for the Ru-based and Ni-based reaction systems, respectively. NH_3 conversion of 99.4% was observed at $T_r = 773$ K for NH_3 flows <100 Nml min^{-1} , whilst it differed marginally (99.8–99.9%) for all GHSV at 873 K. As shown in Fig. 5-3 (b), a general decreasing trend in NH_3 conversion with increasing space velocity was observed and it was more apparent at $T_r = 823$ K. The decreasing trend was attributed to the short contact times of the NH_3 reactant on the catalyst.



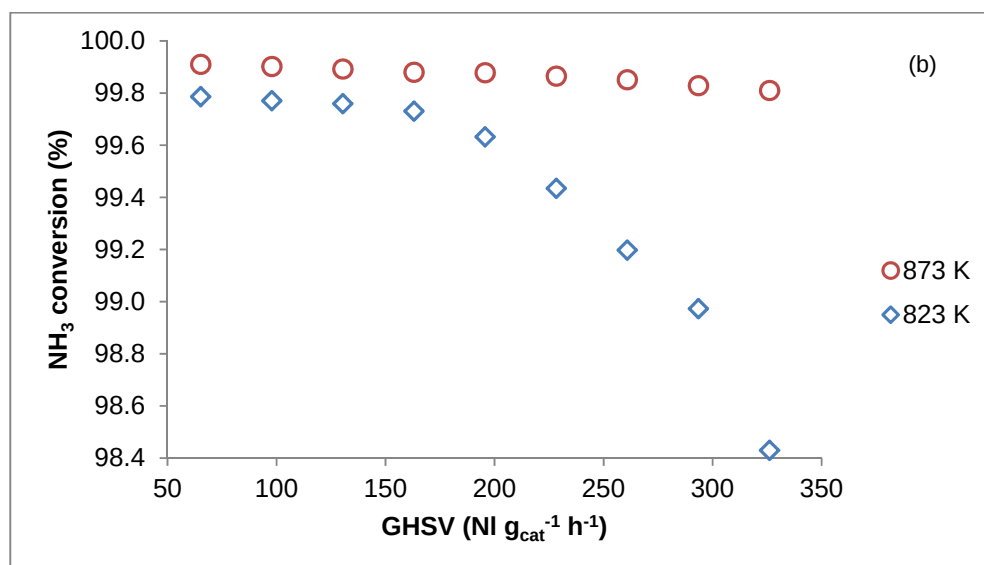


Fig. 5-3 Effect of reaction temperature (a) and space velocity (b) on NH₃ conversion. Experimental conditions: $T_r = 723\text{--}873\text{ K}$, atmospheric pressure, $\text{GHSV} = 65.2\text{--}326.1\text{ NI g}_{\text{cat}}^{-1}\text{ h}^{-1}$.

5.3.3 Effect of reformer temperature and space velocity on hydrogen production

The H₂ production characteristics of the microchannel reformer are illustrated in Fig. 5-4 as a function of space velocities at the lowest and highest reaction temperatures. The specific H₂ production rate was observed to increase with increasing space velocity and reaction temperature. This trend was expected as higher reaction temperatures dictated greater NH₃ conversion and hence faster H₂ production rates particularly at high NH₃ throughput. The highest H₂ production rate was achieved at 873 K and 500 Nml min⁻¹ NH₃ flow. At this operating condition, the reformer achieved a maximum H₂ production rate of 19.9 mol H₂ g_{cat}⁻¹ h⁻¹ corresponding to 1.8 mol h⁻¹. Assuming 60% efficiency of the PEM fuel cell and 80% H₂ utilization [2], an estimated fuel cell power output (Eq. 4) corresponding to 60 W_e was obtained.

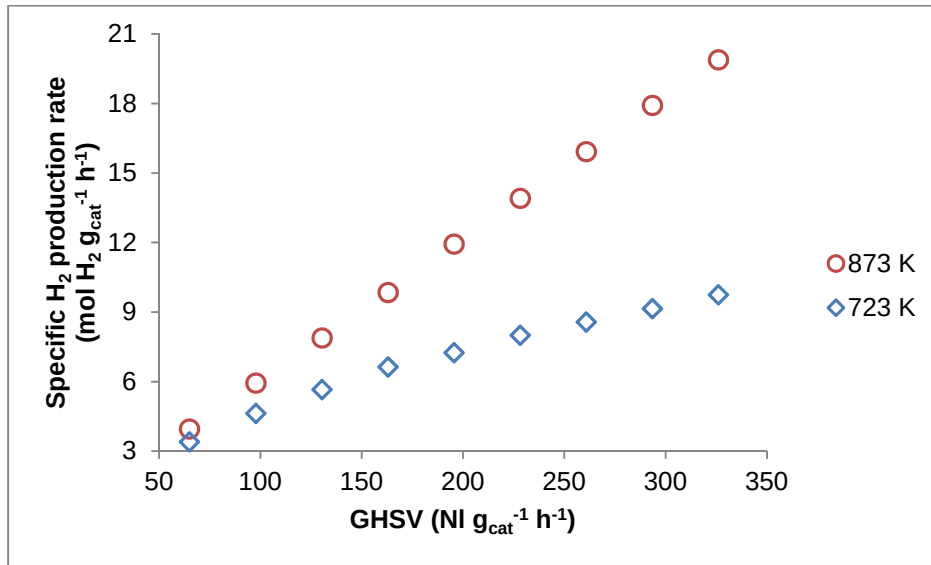


Fig. 5-4 Specific H₂ production rate as a function of space velocity and reaction temperature

5.3.4 Direct comparison with Ni-based microchannel reformer

Based on the present results and those reported in [6], the base case operating conditions for best performance of the stand-alone Ru-based and Ni-based microchannel reactors are summarised in Table 5-1. The Ru-based microchannel reactor used in this work showed an improved performance, and produced ten-fold the reaction rate and power-density rating of the Ni-based micro-reaction system. Chiuta et al. [7] showed that the NH₃ decomposition in the microchannel reformer was reaction-controlled, and internal diffusion limitations within the washcoat were not important. For this reason, the more active Ru-based catalyst produced an improved performance. The lower-temperature performance of the Ru-based system will ensure easier implementation of efficient thermal management strategies which are crucial in the constructing complete NH₃ fuel processors. In addition, the high H₂ throughput exhibited may promote widespread use of the Ru-based micro-reaction system in high-power applications. In this case, the Ru-based system will require less reactors for scale-up to achieve a given power requirement.

Chapter 5: Performance evaluation of a high-throughput microchannel reactor for ammonia decomposition over a commercial Ru-based catalyst

Table 5-1 Summary of base case performance and operating conditions for microchannel reformer

	Microchannel reactor	
	[6]	This work
Feed	Pure NH ₃	
Catalyst	Ni-Pt/ γ -Al ₂ O ₃	Cs-Ru/ γ -Al ₂ O ₃
Catalyst primary metal content (%)	4.7 Ni	8.5 Ru
Reaction temperature (°C)	700	600
Reactor pressure (bara)	0.88	
GHSV (Nl g _{cat} ⁻¹ h ⁻¹)	32.6	326.1
NH ₃ conversion (%)	98.7	99.8
Residual NH ₃ (ppmv)	6 000	1 053
H ₂ production rate (Nml min ⁻¹)	67.5	745.8
Reaction rate (mol _{NH3} g _{cat} ⁻¹ h ⁻¹)	1.3	13.3
Power density (kW _e L ⁻¹)	15.8	163.9
Cold start-up time demand (min)	10	8
Reactor pressure drop (Pa mm ⁻¹)	10	45
Reactor efficiency (%)	14.1	25.5

The Ru-based reactor also produced an H₂-rich reformat with lower residual NH₃ content. The residual NH₃ concentration (1 053 ppmv) however remained well above the permissible limit (100 ppbv [14]) for direct feed into a PEM fuel cell. An adsorbent clean-up unit is therefore required to achieve this limit. Otherwise, the reformat gas may only be fed directly to an Alkaline Fuel Cell (AFC) which is not susceptible to NH₃ poisoning [15]. AFCs' have been dormant for decades but companies such as AFC Energy [16] are resuscitating this technology. The Ru-based reformer produced a maximum pressure drop of 3.3 kPa (45 Pa mm⁻¹). This is higher than the 10 Pa mm⁻¹ attained in [6], yet sufficiently low for NH₃ cylinder pressure (8 bar) to drive flow through the reactor so that operational advantages vis-à-vis reduced balance-of-plant may also be realized. A higher reformer energy efficiency of 25.5% (based on LHV; Eq. 5) was attained by the Ru-based reactor. Kolb [17] reckons that an overall system efficiency of 45% is acceptable for small-scale systems. The development of an integrated (thermally-coupled) ammonia-fuelled microchannel reformer is most likely to increase the efficiency to acceptable levels.

5.3.5 Performance comparison with other ammonia reformers

In Table 5-2, the performance obtained by the microchannel reformer used in the present work was compared with other micro-structured reactors reported in literature for NH_3 decomposition. A fair comparison was difficult owing to the various reaction conditions in different studies. In this study however, the power density was used as the important parameter for comparison. The microchannel reformer used in this work exhibited the best performance, obtaining a power density that exceeded others by at least an order of magnitude. The work reported in [20] used a fixed-bed tubular microreactor filled with a similar Hypermec 10010[®] catalyst. This allowed for the opportunity to compare fixed-bed microreactor vs. microchannel reactor configurations. The microchannel reactor revealed superior catalyst utilisation, achieving approximately the same performance as the fixed-bed microreactor with 40 times less catalyst. The amount of catalyst required in a reactor is influenced by the extent of heat and mass transfer limitations. And so, the attainment of similar NH_3 conversion in a microchannel reactor with less catalyst is indicative of lower heat and mass transport resistances. The microchannel reactor design therefore outperforms the fixed-bed microreactor and is able to draw out the ultimate performance of the Hypermec 10010[®] catalyst. Novakova et al. [21] present similar observations for dehydrogenation of alkanes.

Table 5-2 Comparison of global performance of microstructured reactors for pure NH_3 decomposition

Microreactor Configuration	Catalyst	Reactor volume (cm ³)	Reactor temperature (°C)	NH_3 flow rate (Nml min ⁻¹)	NH_3 conversion (%)	Power density (kW _e L ⁻¹)	Pressure drop (Pa mm ⁻¹)	Ref.
Channel	Ir/Al ₂ O ₃	0.11	900	6	97	6.4	33.3	[9]
Post ^a	Ru/Al ₂ O ₃	0.3	650	50	63	12	-	[18]
Channel	Ru/Al ₂ O ₃	0.35	600	145	99	49.7	-	[10]
Packed-bed ^b	Ru	1.43	650	10	98	0.84	-	[19]
Channel	Ni-Pt/Al ₂ O ₃	0.36	700	50	98.7	15.8	10	[6]
Packed-bed	Cs-Ru/Al ₂ O ₃	15	500	600	99.7	4.7	-	[20]
Channel	Cs-Ru/Al₂O₃	0.36	600	500	99.8	163.9	45	This work

^aPost microreactor

^bPacked-bed microreactor

5.4 Conclusions

The successful application of an ammonia-fuelled microchannel reactor washcoated with a commercial Cesium-promoted Ru/Al₂O₃ catalyst was reported. The best performance was obtained at a reaction temperature of 600 °C and space velocity of 326.1 NI g_{cat}⁻¹ h⁻¹ to produce 99.8% NH₃ conversion and H₂ corresponding to a power density of 164 kW_e L⁻¹. Furthermore, the Ru-based microchannel reactor exceeded the performance of the Ni-based system by an order of magnitude. The high-throughput performance achieved at low-to-medium reaction temperature is adequate to warrant further advances in ammonia fuel processing using micro-reaction technology.

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CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Introduction

This final chapter concludes by presenting a summary of the results and main findings of this study. Furthermore, the implication of these findings to the field of “hydrogen generation via ammonia decomposition” will be presented. Some aspects that need to be addressed by future follow-up studies will also be highlighted.

6.2 Highlights and conclusions

Detailed conclusions were presented at the end of each chapter. This section however recapitulates only the central outcomes (take-home messages) according to the specific objectives of the thesis.

- I. The review of open literature regarding various reactor technologies for pure NH_3 decomposition revealed that microchannel reactors presented an attractive platform to advance NH_3 decomposition as a fuel processing technology for portable and distributed H_2 generation.
- II. The review also exposed the evident lack of the use of an integrated experimental-mathematical modelling approach which is important in obtaining accurate designs of microchannel reactors for NH_3 decomposition.
- III. Miniaturized H_2 production was successfully demonstrated in a microchannel reactor washcoated with a commercial Ni-Pt catalyst for more than 900 h with pleasing stability. The reactor achieved best performance corresponding to an NH_3 conversion and fuel cell power output of 98.7 % and 5.7 W_e , respectively. This performance was obtained at 973 K and 50 Nml min^{-1} NH_3 flow. The Ni-Pt microchannel reactor was found to be more suitable for low-power fuel cell applications.

- IV. For the entire operating space used in the evaluation of the Ni-Pt microchannel reactor, the residual NH_3 concentration exceeded the PEM fuel cell tolerance limit (6 000 ppm vs. 0.1 ppm). Consequently, direct feed of the H_2 -rich reformat gas to the PEM fuel cell without a clean-up unit is not recommended. Nonetheless, the design-point residual NH_3 concentration is the prerogative of the intended operator based on definite trade-offs i.e. low residual NH_3 is achieved at a penalty of low H_2 productivity (low fuel cell power output).
- V. A 3D mathematical model was successfully developed using the finite element based Comsol Multphysics™ simulation software. The model extensively delineated the reaction-coupled transport phenomena (reactive flow, heat, and mass transfer) occurring within the microchannel reactor.
- VI. The 3D mathematical model results were in good agreement with experimental data obtained from the Ni-Pt microchannel reactor over a wide range of the experimental parameter space. The model therefore adequately captured the performance of the experimental Ni-Pt microchannel reactor.
- VII. High-throughput NH_3 decomposition was successfully demonstrated using the Ru-based microchannel reactor. An NH_3 conversion of 99.8% was achieved at 873 K and 500 Nml min^{-1} NH_3 flow. The H_2 produced from the single reactor was sufficient to power a fuel cell of rating 60 W_e .
- VIII. The Ru-based microchannel reactor used in this work showed an improved performance, exceeding the power-density rating of the Ni-based microchannel reactor by an order of magnitude (ten-fold). In addition, the Ru-catalyzed microchannel reactor produced an H_2 -rich reformat with less residual NH_3 than the Ni-Pt catalyzed microchannel reactor (1 050 ppm vs. 6 000 ppm).

6.3 Contribution to current knowledge

The following achievements were considered valuable contributions to current knowledge on H_2 generation via NH_3 decomposition:

- I. Chapter 2 of this thesis (A review) was a valuable contribution in that it presented for the first time a condensed viewpoint and analysis concerning the state-of-the-art reactor technologies for distributed H_2 generation via NH_3 decomposition. Specifically, the work outlined the pros and cons, as well as uncovered the technology gaps of the various reactor technologies all to present an important platform for future research.
- II. The experimental work in Chapters 3 and 5 demonstrated the successful design, construction and operation of stand-alone ammonia-fuelled microchannel reactors. A significant aspect of this work was the evaluation of the performance of these microchannel reactors under daily start-up and shutdown conditions to mimic the practical intermittent operation of fuel cells. Overall, this work was an important extension to the limited literature available regarding experimental investigations of ammonia-fuelled microchannel reactors.
- III. Chapter 4 demonstrated the use of an integrated experimental-mathematical modelling approach for the efficient development of ammonia-fuelled microchannel reactors for H_2 generation. The vital features of this important approach included CFD model development, extensive model validation (direct), parameter sensitivity analysis and parameter-identification for best operating space. An important contribution was the direct validation and agreement of the CFD model results with experimental data for the stand-alone ammonia-fuelled microchannel reactor. In addition, the CFD model developed offered a thorough insight into the fundamental operation of the microchannel reactor.

6.4 Recommendations for future work

While this thesis focused on the development and application of a fundamental approach useful in designing ammonia-fuelled microchannel reactors, there is significant research scope that still needs to be exploited before the breakthrough of ammonia-fuelled microchannel reactors into the hydrogen and fuel cell market. The possible research prospects are outlined in this section:

- I. Whilst case-study optimization was used in this thesis to identify the best design and operating parameters of the stand-alone ammonia-fuelled microchannel reformer, a systematic optimization study (using non-linear programming techniques e.g. SNOPT) should be considered in order to define the optimum parameters with improved accuracy.
- II. Detailed characterization of the porous washcoat catalyst to obtain accurate parameters such as porosity, permeability, active surface area and dispersion should be considered. In addition, an experimental kinetic study of the Hypermec 10010 Ru catalyst used should be done with the objective of obtaining reliable kinetics for subsequent modelling of the Ru-based microchannel reactor.
- III. An integrated (thermally-coupled) ammonia-fuelled microchannel reformer is most likely to increase the efficiency to acceptable levels (>45%). In this case, the endothermic NH_3 decomposition is coupled to an exothermic reaction occurring on the same microdevice substrate in order to achieve a self-sustaining heat recirculation operation. Modelling and experimental studies are required specifically to answer crucial questions regarding efficient heat recirculation.
- IV. A useful study to consider will also be to demonstrate and characterize coupled operation of an integrated microchannel reactor with a clean-up unit and a PEM fuel cell stack. How is the fuel cell performance (power output) affected by microreactor

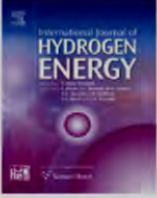
operation? In addition, dynamic modelling and experimental validation are required to identify practical operational concerns as well as devise efficient strategies for fast start-up.

APPENDIX A: TITLE PAGES OF PUBLISHED ARTICLES

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Review

Reactor technology options for distributed hydrogen generation via ammonia decomposition: A review

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ARTICLE INFO	ABSTRACT
Article history: Received 3 July 2013 Received in revised form 13 September 2013 Accepted 13 September 2013 Available online 9 October 2013 Keywords: Reactor infrastructure Ammonia decomposition Distributed hydrogen generation PEM fuel cell	Hydrogen (H₂) fuel obtained via thermo-catalytic ammonia (NH₃) decomposition is rapidly attracting considerable interest for portable and distributed power generation systems. Consequently, a variety of reactor technologies are being developed in view of the current lack of infrastructure to generate H₂ for proton exchange membrane (PEM) fuel cells. This paper provides an extensive review of the state-of-the-art reactor technology (also referred to as reactor infrastructure) for pure NH₃ decomposition. The review strategy is to survey the open literature and present reactor technology developments in a chronological order. The primary objective of this paper is to provide a condensed viewpoint and basis for future advances in reactor technology for generating H₂ via NH₃ decomposition. Also, this review highlights the prominent issues and prevailing challenges that are yet to be overcome for possible market entry and subsequent commercialization of various reactor technologies. To our knowledge, this work presents for the first time a review of reactor infrastructure for distributed H₂ generation via NH₃ decomposition. Despite commendable research and development progress, substantial effort is still required if commercialization of NH₃ decomposition reactor infrastructure is to be realized. Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

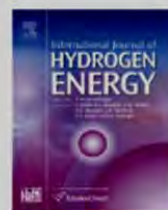
1. Introduction

The world today faces critical challenges defined by gradually depleting non-renewable fossil fuel reserves and the likelihood of global warming in the wake of a rapidly growing global population. These simultaneous challenges threaten an energy and environmental crisis that is expected to have far-reaching socio-economic consequences. The predicament is

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Experimental performance evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation

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ABSTRACT

Microchannel reactors appear attractive as integral parts of fuel processors to generate hydrogen (H_2) for portable and distributed fuel cell applications. The work described in this paper evaluates, characterizes, and demonstrates miniaturized H_2 production in a stand-alone ammonia-fuelled microchannel reformer. The performance of the microchannel reformer is investigated as a function of reaction temperature (450–700 °C) and gas-hourly-space-velocity (6520–32,600 $Nml\ g_{cat}^{-1}\ h^{-1}$). The reformer operated in a daily start-up and shut-down (DSS)-like mode for a total 750 h comprising of 125 cycles, all to mimic frequent intermittent operation envisaged for fuel cell systems. The reformer exhibited remarkable operation demonstrating 98.7% NH_3 conversion at 32,600 $Nml\ g_{cat}^{-1}\ h^{-1}$ and 700 °C to generate an estimated fuel cell power output of 5.7 W_e and power density of 16 $kW_e\ L^{-1}$ (based on effective reactor volume). At the same time, reformer operation yielded low pressure drop ($<10\ Pa\ mm^{-1}$) for all conditions considered. Overall, the microchannel reformer performed sufficiently exceptional to warrant serious consideration in supplying H_2 to fuel cell systems.

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Introduction

Fuel cells are fast gaining extensive interest for portable and distributed power generation systems. Their exceptional operational characteristics such as high power densities, quiet operation, and inherent ability to generate near-zero pollution

make them particularly attractive for a world experiencing simultaneous energy and environmental sustainability challenges [1,2]. The potential for widespread adoption of fuel cell technology however remains subdued owing to several significant techno-economic obstacles. Principally, the low volumetric energy density of hydrogen (H_2) effect storage and transportation difficulties, which create a wide gap in the H_2

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A modelling evaluation of an ammonia-fuelled microchannel reformer for hydrogen generation

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ABSTRACT

Hydrogen production from an ammonia-fuelled microchannel reactor is simulated in a three-dimensional (3D) model implemented via Comsol Multiphysics™. The work described in this paper endeavours to obtain a mathematical framework that provides an understanding of reaction-coupled transport phenomena within the microchannel reactor. The transport processes and reactor performance are elucidated in terms of velocity, temperature, and species concentration distributions, as well as local reaction rate and NH₃ conversion profiles. The baseline case is first investigated to comprehend the behaviour of the microchannel reactor, then microstructural design and operating parameters are methodically altered around the baseline conditions to explore the optimum values. The simulation results show that an optimum NH₃ space velocity (GHSV) of 65,000 Nm³ g⁻¹ h⁻¹ yields 99.1% NH₃ conversion and a power density of 32 kW_e L⁻¹ at the highest operating temperature of 973 K. It is also shown that a 40-μm-thick porous washcoat is most desirable at these optimum conditions. Finally, a low channel hydraulic diameter (225 μm) is observed to contribute to high NH₃ conversion. Mass transport limitations in the porous-washcoat and gas-phase are negligible as depicted by the Damköhler and Fourier numbers, respectively. The experimental microchannel reactor yields 98.2% NH₃ conversion and a power density of 30.8 kW_e L⁻¹ when tested at the optimum operating conditions established by the model. Good agreement with experimental data is observed, so the integrated experimental-modelling approach developed in this paper may well provide an incisive step toward the efficient design of ammonia-fuelled microchannel reformers.

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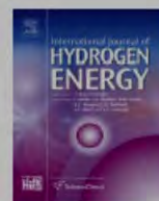
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Short Communication

Performance evaluation of a high-throughput microchannel reactor for ammonia decomposition over a commercial Ru-based catalyst



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ABSTRACT

In this work, the prospect of producing hydrogen (H_2) via ammonia (NH_3) decomposition was evaluated in an experimental stand-alone microchannel reactor wash-coated with a commercial Ruthenium-based catalyst. The reactor performance was investigated under atmospheric pressure as a function of reaction temperature (723–873 K) and gas-hourly-space-velocity (65.2 – $326.1\text{ NL g}_{cat}^{-1}\text{ h}^{-1}$). Ammonia conversion of 99.8% was demonstrated at $326.1\text{ NL g}_{cat}^{-1}\text{ h}^{-1}$ and 873 K. The H_2 produced at this operating condition was sufficient to yield an estimated fuel cell power output of 60 W_e and power density of $164\text{ kW}_e\text{ L}^{-1}$. Overall, the microchannel reactor considered here outperformed the Ni-based micro-structured system used in our previous work.

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Introduction

The low volumetric energy density of hydrogen (H_2) fuel is widely considered the primary constraint in deploying fuel cell technology at a large scale. At present, there exists a wide gap in the H_2 supply chain to advance fuel cells to extensive

commercialisation. Hardman and Steinberger-Wilckens [1] mention that successful infrastructural pre-development is essential in attaining a viable H_2 economy. On the foregoing, the existing lack of an adequate infrastructure motivates the need for on-site generation of H_2 via reforming of alternative H_2 carriers in fuel processors [2]. Among the various options, ammonia (NH_3) decomposition has lately been receiving

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APPENDIX B: SUPPLEMENTARY LITERATURE

B.1 Setting the scene for a hydrogen economy

Energy has been an integral part of human civilization since time immemorial. Over the years, the demand for energy has been increasing owing to an ever-increasing global population and technological advances. Until today, fossil fuels have been at the heart of energy supply worldwide. However, there is a growing concern with regards to the potentially finite fossil fuel reserves. There are also growing concerns worldwide about global warming, linked with greenhouse gases (e.g., methane and carbon dioxide emissions) from fossil fuels. The lack of balance between energy supply and demand as well as environmental degradation issues requires a rethink to ensure a sustainable economy for the future. Hence, the world today is seeking to minimize the dependence on crude oil by achieving higher efficiency on the existing usage and exploring greener alternatives for the future.

Use of hydrogen, resulting in water as the only byproduct, provides an ideal, environmentally benign fuel for the future, replacing the carbon based energy sources of today. The journey towards a hydrogen economy, which began with the quest for higher efficiency and eco-friendly systems, is now accelerated by the rising oil prices, and the need for energy independence. In realizing a hydrogen economy, hydrogen can be burnt (oxidized) in internal combustion engines and gas turbines (replacing conventional fossil fuels) for cleaner energy production (zero carbon emissions). Alternatively, hydrogen can also be burnt catalytically or electrochemically (i.e., using fuel cells (FCs)) further eliminating NO_x emissions. Given their high fuel-to-electricity efficiency, hydrogen based FC systems are thought to hold the key to a sustainable future.

B.2 Recent interest in fuel cells for power generation

Fuel cells have been known since their invention in 1839 by Sir William Grove. However, their incorporation into consumer devices was conceived of only recently. Recent interest in fuel cells

is motivated by efficiency considerations. Fuel cells are more efficient than combustion processes owing to the fact that chemical energy (from hydrogen) is directly transformed to electrical energy without going via combustion. Various types of FCs, such as proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC), direct methanol fuel cells (DMFC) are being developed for specialized applications. The incorporation of the FC technologies into different areas, such as transportation, regenerative power and portable power, is steadily gaining momentum with many companies driving the technology towards commercialization.

B.2.1 Fuel cells in automotive transport applications

One application that has received much attention is transportation, especially for use in cars and buses. Local pollution in urban areas is an important factor in this regard. Legislative initiatives like the US Clean Air Act and similar initiatives in California have brought about more focus on low emission vehicles from the car manufacturers. Nearly all major car manufacturers have programs in place for FC vehicles. One obstacle for large scale market penetration of FC vehicles is the efficient distribution of an appropriate fuel for FCs in cars.

B.2.2 Fuel cells in premium and distributed power applications

Premium power applications for powering portable electronics and power back-up for large computer systems may also be interesting for fuel cells. Polymer electrolyte membrane fuel cells (PEMFCs) have been proposed as battery replacements and for use in hybrid fuel cell battery systems to augment the battery's energy density. Hydrogen-fueled portable power sources are gaining interest for both civilian and military applications (Holladay et al., 2004). These novel power sources, which combine a fuel processor with a FC, harness the high energy density of hydrocarbon and other alternative fuels. Coupled with the high efficiencies of the FCs, this route offers a potential to surpass the performance of the state-of-the-art Li-ion batteries by providing higher energy densities, which result in enhanced operational time (by a factor of 10-100) or lighter devices (Jones et al., 1999). The higher energy densities of FCs and easier implementation of recharging procedures make FCs more competitive than battery

technologies for portable applications. Distributed energy is also an attractive technology as it allows for on-site energy conversion and power generation at many locations on a network of energy sources.

In all these applications, for example, a fuel cell system will be coupled to a fuel processor to generate hydrogen fuel on demand. These systems will require small, light, and compact components, so that microscale devices are necessary for their implementation. Microstructured chemical devices, which produce hydrogen, and micro FCs, which generate electricity, would be integral components of future hydrogen-based power generators. The focus of this thesis is the development of hydrogen-producing microchemical devices. In the subsequent sections, the features and limitations of microstructured chemical devices are discussed, and then the hydrogen production routes reviewed.

B.3 Microstructured reactors

Microstructured reactors, also called microreactors, are miniaturized reaction systems that are produced using methods of microtechnology or precision engineering (Ehrfeld et al., 2000). Typically, microreactors contain fluid channels with a diameter between 10 and 500 μm , which results in a relatively large surface area-to-volume ratio and increased driving forces for heat and mass transport (Lowe & Ehrfeld., 1999; Jensen., 2001). One of the first microstructured devices was reported in literature in 1989 (Schubert., 1989). Microreactor Engineering has been recognized as a new discipline since the first workshop on Microsystems Technology for Chemical and Biological Microreactors, held in Germany in 1995 (Ondrey., 1995). Since then many research groups have entered the field. Several reviews of the field have already appeared in books and papers (Ehrfeld et al., 1999; Ehrfeld et al., 2000; Gavriilidis et al., 2000; Hessel et al., 2004).

B.3.1 Advantages of microstructured reactors

Due to their small diameter, microchannels have very good heat and mass transfer properties. Therefore, the rate of reactions that are limited by heat or mass transfer in a conventional reactor, can be increased by performing the reaction in a microreactor, leading to process intensification (Stankiewicz & Moulijn., 2000). Furthermore, nonuniformities in temperature (in the case of fast, highly exothermic reactions) or concentration (when the reactants have to be mixed in the reactor) can be avoided in a microreactor, which can result in improved selectivity and yield. The temperature uniformity also makes microreactors well suited for measuring intrinsic reaction kinetics (Besser et al., 2002; Rebrov et al., 2003).

Microchannels also have a small volume. When used as a measurement or analysis device, this leads to less consumption of space, materials, and energy, and, in combination with fast heat and mass transfer, also to a shorter analysis time (Manz et al., 1990). These qualities resulted in a large interest in microreactors for high throughput experimentation (Zech & Honicke., 2000; Muller et al., 2002). The small inventory also makes microreactors safer for handling dangerous chemicals (Hendershot., 2000). The flame arrestor capabilities of the small channels can be used to make an intrinsically safe reactor for handling explosive reaction mixtures (Janicke et al., 2000; Vesper., 2001). This enables performing reactions under conditions that used to be inaccessible and that might lead to increased selectivity and yield and can avoid the use of large diluent streams.

A third microreactor property is its modular nature. Scaling-up a process by using a large number of small units, identical to those used in the laboratory, avoids the uncertainties involved in the design of a new process or, in case of a pharmaceuticals product, avoids a lengthy new licensing procedure, which can significantly shorten the time-to-market of a new product (Ehrfeld., 1999). Furthermore, the modular nature of microreactors also facilitates distributed production, where (possibly dangerous) chemicals are being made at the place where they are

needed, in this way avoiding the transportation risks and costs (Benson & Ponton., 1993; Ajmera et al., 2001).

B.3.2 Differences between microstructured and conventional reactors

Microreactors also differ from conventional reactors in a number of ways. The main differences between microreactors and macro-scale equipment are:

1. The flow in microstructures is often laminar, whereas flow in macro-scale equipment is usually turbulent
2. Heat and mass transfer across boundaries is very fast in microreactors, while it is often a limiting factor in conventional reactors.
3. The volume fraction of solid wall material is much higher in microreactors than in macroscopic equipment, which makes solid heat conduction an important factor in microreactors, while it can usually be neglected in conventional reactors.
4. Small reactors are more sensitive to their outside environment than larger units.
5. The large surface area-to-volume ratio of the microstructures results in an increased importance of surface effects over volumetric effects.

B.3.3 Design challenges and limitations for microstructured reactors

Despite the advantages of microchemical devices, certain practical criteria need to be met before portable microreaction devices are realized. Firstly, the energy losses associated with the operation of ancillary equipment, such as pumps or compressors, need to be minimized using low pressure drop designs. Secondly, incomplete reactant conversions not only imply underutilized resources but also more downstream processing, resulting in lower efficiencies. Hence, devices with adequate catalyst loadings, residence times, and reactant contact (mixing) need to be designed.

For ammonia decomposition, the microreactor also needs to meet the DOE standards regarding NH_3 conversion, cold startup time, cost, and transient response (Thomas & Parks.,

2006). Figure B-1 shows the DOE targets in terms of the volume of ammonia fuel and the reactor size or footprint for a 5 kg hydrogen production unit as a function of ammonia conversion. It is clear from the graph that designing compact microreactors with high conversions is critical to meet these stringent process targets. Optimal microreactor design is essential in order to meet these criteria. In view of this, the development of mathematical reactor models is an important aspect for the reliable design and optimization of microreactors. Therefore, an experimental and mathematical modelling approach is undertaken in this thesis as a first step to obtain accurately optimized designs for ammonia-fuelled microchannel reactors.

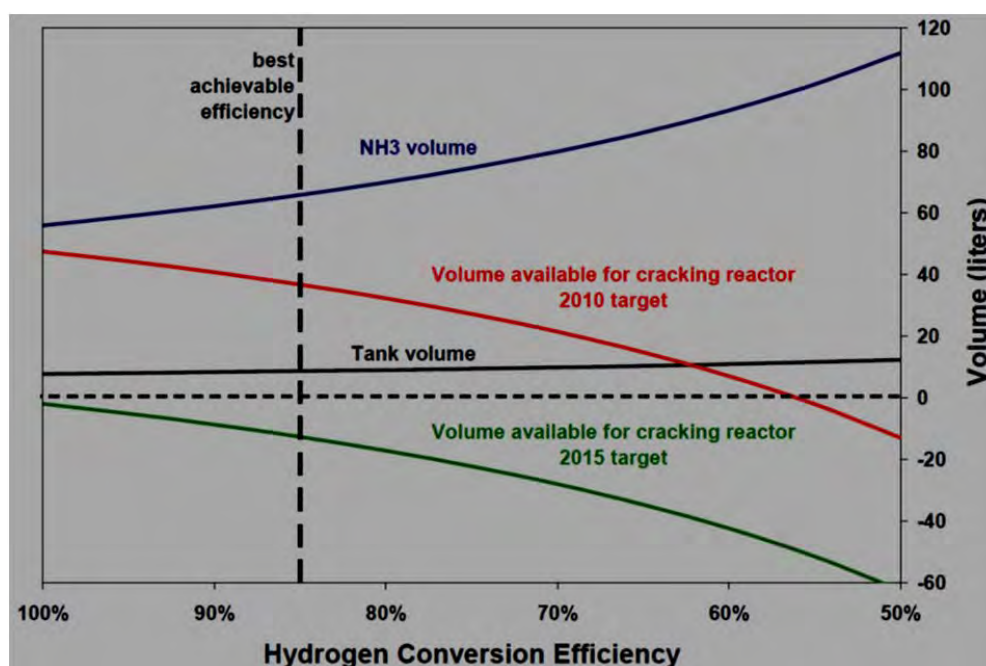


Figure B-1 Ammonia conversion and system volume targets for an ammonia cracker capable of producing 5 kg of H₂ based on the DOE FreedomCAR. High catalytic activity compact devices are desirable to meet these targets.
Adapted from Thomas and Parks (2006)

B.3.4 Fabrication of microstructured devices

A number of fabrication techniques meet the general requirements for constructing an efficient and compact microreactor. Popular methods include LIGA, wet and dry etching processes, micromachining, lamination, and soft lithography.

B.3.4.1 LIGA

The LIGA technique was primarily developed by researchers in Germany, with Forschungszentrum Karlsruhe and the Institute for Microtechnology Mainz (IMM) being the primary drivers (Ehrfeld et al., 2000). This process combines deep lithography, electroplating, and molding using three general steps (Tonkovich et al., 2001). The first step is the pattern transfer using a serial beam writing process or mask into a photoresist or a special photosensitive epoxy, such as SU8, deposited on an electrically conductive substrate. After any undesirable material is removed (e.g., the mask is developed), a relief structure is formed by electroplating onto the exposed substrate areas. Once the metallic structure is formed, the resist or epoxy is removed. In some instances, this metallic structure may be the final product; however, usually it is used as a master tool for a replication process (such as injection molding, casting, or embossing), which is the final step in the process.

B.3.4.2 Wet and Dry Etching Processes

Wet and dry etching processes have largely been developed for the semiconductor industry. Wet etching uses a liquid etch solution (such as potassium hydroxide to etch silicon) to remove unwanted material from the substrate anisotropically, whereas dry etching tends to use plasmas or reactive plasmas and may be anisotropic or isotropic, depending on the plasma source (Holladay et al., 2004). Similar to dry etching is deep reactive ion etching (DRIE), which is often used in the fabrication of microelectromechanical systems (MEMS). Since wet etching is an anisotropic process, it has strong restrictions on the geometries that can be made. Isotropic dry etching enables a wider variety of geometries but is more limited in the materials that can be etched. The initial step in the process is the same as that of LIGA; specifically, a pattern is transferred into a photoresist or other protective layer. The unprotected substrate areas are etched using either technique. Next, the protective layer is removed. To make the final device, several substrates fabricated using this method are stacked on top of each other.

B.3.4.3 Micromachining

In contrast to LIGA and wet/dry etching, the three main processes for micromachining shapes typically do not need the initial deposition of a resist, epoxy, or other protective layers. The equipment also tends to be less expensive for purchasing and maintenance. While not required, these processes are often computer controlled. The first technique involves traditional milling, turning, and grinding, but with ultraprecision machines that produce small features (Ehrfeld et al., 2000; Tonkovich et al., 2001). The feature sizes are not as small as those constructed from LIGA and other fabrication processes; however, almost any material can be used. The second technique uses laser radiation to remove material or, in some situations, to build up material. The most common procedure is to remove material by melting, evaporation, decomposition, photoablation, or a combination of these removal techniques.

Some development involves building structures by photochemically cross-linking in organic compounds or powder solidification by laser sintering. Both processes can be used to make devices down to critical dimensions of approximately 10 μm ; however, the surfaces tend to be rough, which may cause problems in some cases (Ehrfeld et al., 2000). The third technique is electrodischarge machining (EDM), also called micro-electrodischarge machining. This technique is limited to electrically conductive work pieces. Material is removed by small sparks in a dielectric fluid, such as deionized water or oil, between the work piece and an electrode. The main disadvantages of this type of machining are relatively rough surfaces; limitations in miniaturization to the size of the electrodes and spark; and relatively long machining times, which may limit the technology to prototyping and manufacture of mold inserts (Ehrfeld et al., 2000).

B.3.4.4 Lamination

In a lamination process, several sheets with different patterns are stacked and then brazed or bonded together. In a MEMS-based approach, DRIE is used to make patterns in silicon or other materials. The substrates are then stacked and bonded together using silicon

bonding methods developed for MEMS. Another approach, used by researchers at Pacific Northwest National Laboratory (Tonkovich et al., 2001) is the fabrication of thin metal laminates using stamping, embossing, or processes described previously. These laminates are then stacked and brazed or diffusion bonded into a single device (Ameel et al., 2000; Tonkovich et al., 2001). Lamination is also particularly well suited for fabricating ceramic devices. Ceramic tapes, in the soft, pliable “green state”, are cut, molded, laser cut, and so forth to the desired design and stacked. After curing in high-temperature furnaces, the laminates are bonded into a single structure.

B.3.4.5 Soft Lithography

Whitesides and coworkers developed a collection of lithographic techniques referred to as soft lithography (Ameel et al., 2000). An elastomer, often poly(dimethylsiloxane), with a pattern embossed on its surface, is used to transfer the pattern onto the substrate (often by stamping). This technique is used in biological applications but can be combined with other polymers, electroplating techniques, or molding of ceramics for low-cost, fast prototyping of devices (Ameel et al., 2000; Tonkovich et al., 2001).

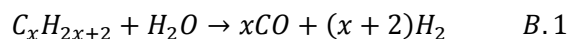
B.4 Fuel processing routes for production of hydrogen on-demand

Conventional hydrogen storage technologies may not be the best solution for portable power generation owing to the low hydrogen storage density of all the established technologies. Consequently, there is great interest in exploring methods of producing hydrogen on-demand from easily stored liquid fuels such as gasoline, diesel, methanol, or ammonia. Oftentimes, the hydrogen production must be accompanied by additional steps to prepare the fuels for the hydrogen-generating reactions, to ensure that additional by-products do not interfere with fuel cell operation, and that the reactions do not produce harmful emissions. All of the steps including hydrogen generation itself are referred to as fuel processing.

Hydrogen can be produced in a great number of ways. The various methods of producing hydrogen are described in several review articles (Dicks., 1996; Pena et al., 1996; Armor., 1999;). The preferred method of production on an industrial scale is steam reforming of hydrocarbons. This method has proved to be the most economical option in large scale hydrogen production, but it is unclear whether or not this will be the best chemistry at the small scale. In stationary applications, conversion efficiency and cost are the main considerations. At the small scale, however, size, weight, response time, and system complexity, in addition to conversion efficiency and cost must be considered.

B.4.1 Steam reforming of hydrocarbons and alcohols

Steam reforming of hydrocarbons is considered by many to be the most practical and economical way to produce hydrogen on the large scale. This process involves several reactions. First, there is the reaction of the hydrocarbon with steam to generate carbon monoxide and hydrogen (syngas):



Since this reaction is highly endothermic, it is carried out at high temperatures (between 750 and 1000 °C over Nickel catalysts for methane, for example) to achieve high conversions. Excess steam is also typically used to prevent excessive carbon formation (coking) on the catalyst. The heat of reaction is usually provided by combusting a fraction of the fuel in air. Reaction B.1 is followed by the water-gas-shift (WGS) reaction to produce more hydrogen at the same time generating carbon dioxide in the process:



This reaction is reversible and slightly exothermic. Hence, the forward reaction is favoured at low temperatures. Industrially, this is attained in two steps. First, the syngas is reacted over a chromium-promoted iron oxide catalyst in a high-temperature shift (HTS) reactor

with an inlet temperature of 370 °C. The product gases are then sent to a low-temperature shift reactor at about 200 °C to react over a copper-zinc oxide catalyst (Armor., 1999).

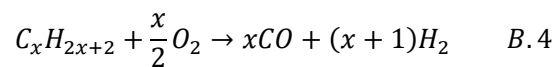
Steam reforming can also be carried out using alcohols. Methanol is a commonly studied fuel for steam reforming in portable fuel processors. Methanol can be stored easily as a liquid, and methanol reforming can be carried out at low temperatures (typically 200–300 °C) over zinc-oxide supported copper catalysts. The overall reaction for methanol reforming is:



Regardless of the fuel that is used, the product gas (reformat) from the steam reforming reaction will contain a finite concentration of CO. The low-temperature shift reactors will reduce the CO level down to approximately 1%, but to achieve lower levels of CO, further processing is necessary. A PEMFC requires CO levels in the ppm range in the feed to prevent poisoning the Pt electrocatalyst.

B.4.2 Partial oxidation of hydrocarbons and alcohols

An alternative to steam reforming is partial oxidation. Partial oxidation of hydrocarbons can be achieved by combining the fuel with less than the stoichiometric amount of oxygen required for complete combustion (equivalence ratio less than one) to produce syngas. The partial oxidation of hydrocarbons is described by:



Steam reforming produces more hydrogen per mole of fuel (as hydrogen is extracted from the steam as well as the fuel), but partial oxidation offers one major advantage that may make it more attractive for portable hydrogen generation. It is a single exothermic reaction, which means that, unlike steam reformers, thermal coupling is not required. This could lead to much simpler and compact devices.

B.4.3 Thermal decomposition

Another option for hydrogen production is thermal decomposition, also known as cracking. Cracking can be carried out using hydrocarbon fuels, though this results in the formation of carbon with the hydrogen. Alternatively, ammonia cracking can also be carried out, which results in the formation of nitrogen and hydrogen.

B.4.3.1 Hydrocarbon cracking

Thermal decomposition of hydrocarbons yield solid carbon and hydrogen, and is an endothermic process. Homogeneous cracking of hydrocarbons requires temperatures in excess of 1000 °C. However, catalytic cracking of hydrocarbons can be carried out at lower temperatures. The disadvantage is that catalytic hydrocarbon cracking will always lead to carbon deposition (coking) on the catalyst. This will require the catalyst to be periodically regenerated so that this process is inherently transient. The implementation of a hydrocarbon cracker for small scale hydrogen production may be difficult. The temperatures required for hydrocarbon cracking are very high, and heat management in such a system may be very difficult. In addition, to de-carbon the catalyst would require a complicated control system for periodic valve switching. And, such a system is likely to be bulky and energy intensive for a power generator at the small scale.

B.4.3.1 Methanol cracking

Methanol decomposition is an alternative to hydrocarbon decomposition that does not necessarily lead to carbon deposition on the catalyst. The overall reaction for methanol decomposition is as follows:



This reaction is typically performed over transition metal catalysts (Ni, Pd, Cu) at temperatures around 400 °C (Pena et al., 1996). Using these catalysts, carbon formation is not a significant side reaction. Methanol decomposition is much more attractive for portable hydrogen generation than hydrocarbon cracking, given that it can operate steadily without the

need to regenerate catalyst. However, the methanol decomposition produces 2 moles of hydrogen per mole of methanol, whereas methanol steam reforming produces 3 moles of hydrogen per mole of methanol. In addition, about 33 mol% CO is produced in the product gas for methanol decomposition. Therefore, there are no clear advantages of methanol decomposition over methanol steam reforming.

B.4.3.1 Ammonia cracking

Ammonia decomposes into nitrogen and hydrogen according to the reaction B.6. Ammonia decomposition is typically performed over supported metal catalysts. Unlike steam reforming of hydrocarbons, the product gas of the ammonia decomposition reaction does not contain CO. The nitrogen in the product stream only acts as a diluent affecting only the power density of the fuel cell. On the other hand, the residual ammonia can affect the fuel cell performance, as it may preferentially adsorb on the Pt electrocatalysts in the PEMFC. Any unreacted ammonia therefore needs to be scrubbed off from the fuel cell feed. However, ammonia cracking is a promising method to deliver hydrogen to a portable PEMFC. The base case for ammonia cracking have been extensively deliberated in Chapter 2 of this thesis.



Table B-1 Basic physical properties of ammonia

Hydrogen Content					
Hydrogen weight fraction	17.65	wt. %	Hydrogen volume density	0.105	kg/liter
Solid Phase					
Melting point	-78	°C	Latent heat of fusion (1 atm at triple point)	-337.37	kJ/kg
Liquid Phase					
Vapor pressure (21°C)	8.88	bar	Liquid density (1 atm @ boiling point)	682	kg/m ³
Boiling point (@ 1.0 atm)	-33.5	°C	Liquid/gas equivalent (1 atm and 15°C)	947	vol/vol
Latent heat of vaporization (1 atm @ boiling point)	1371.2	kJ/kg			
Critical temperature	132.4	°C	Critical pressure	112.8	bar
Gas Phase					
Gas density (1 atm at boiling point)	0.86	kg/m ³	Gas density 15°C 1 atm	.73	kg/m ³
Compressibility (Z) (1 atm at 15°C)	.9929		Specific gravity (air=1) (1 atm at 20°C)	.597	
Specific volume 1 atm at 20°C)	1.411	m ³ /kg	Viscosity	.000098	Poise
Heat capacity at constant pressure (Cp) (1 atm at 15°C)	.037	kJ/(mol.K)	Heat capacity at constant volume (Cv) (1 atm at 15°C)	.028	kJ/(mol.K)
Critical Density:	0.24	g/ml	Entropy, Gas @ 25°C., 1 atm. :	45.97	cal/mol°C
Thermal conductivity	22.19	mW/(mK)			
Miscellaneous					
Water solubility (1 atm at 0°C)	862	vol/vol	Auto ignition temperature	630	°C
Lower flammable limit in air	15%	by volume	Upper flammable limit in air	28%	by volume
Molecular Weight:	17.03				

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APPENDIX C: SAMPLE EXPERIMENTAL PRODUCTION DATA SHEET

Table C-1 Sample experimental data recording sheet

Time (h)	Set-point reactor temp (°C)	Feed temp (°C)	NH ₃ flow rate (Nml/min)	GHSV (Nml/g _{cat} h)	Pressure drop (Pa)	Temp. 1 (°C)	Temp. 2 (°C)	NH ₃ mole fraction	H ₂ mole fraction	N ₂ mole fraction	Reformat flow rate (Nml/min)
0.5											
1.0											
1.5											
2.0											
2.5											
3.0											
3.5											
4.0											
4.5											
5.0											
5.5											
6.0											

APPENDIX D: REFORMATE GAS COMPOSITION FOR Ni-Pt MICROREACTOR SYSTEM

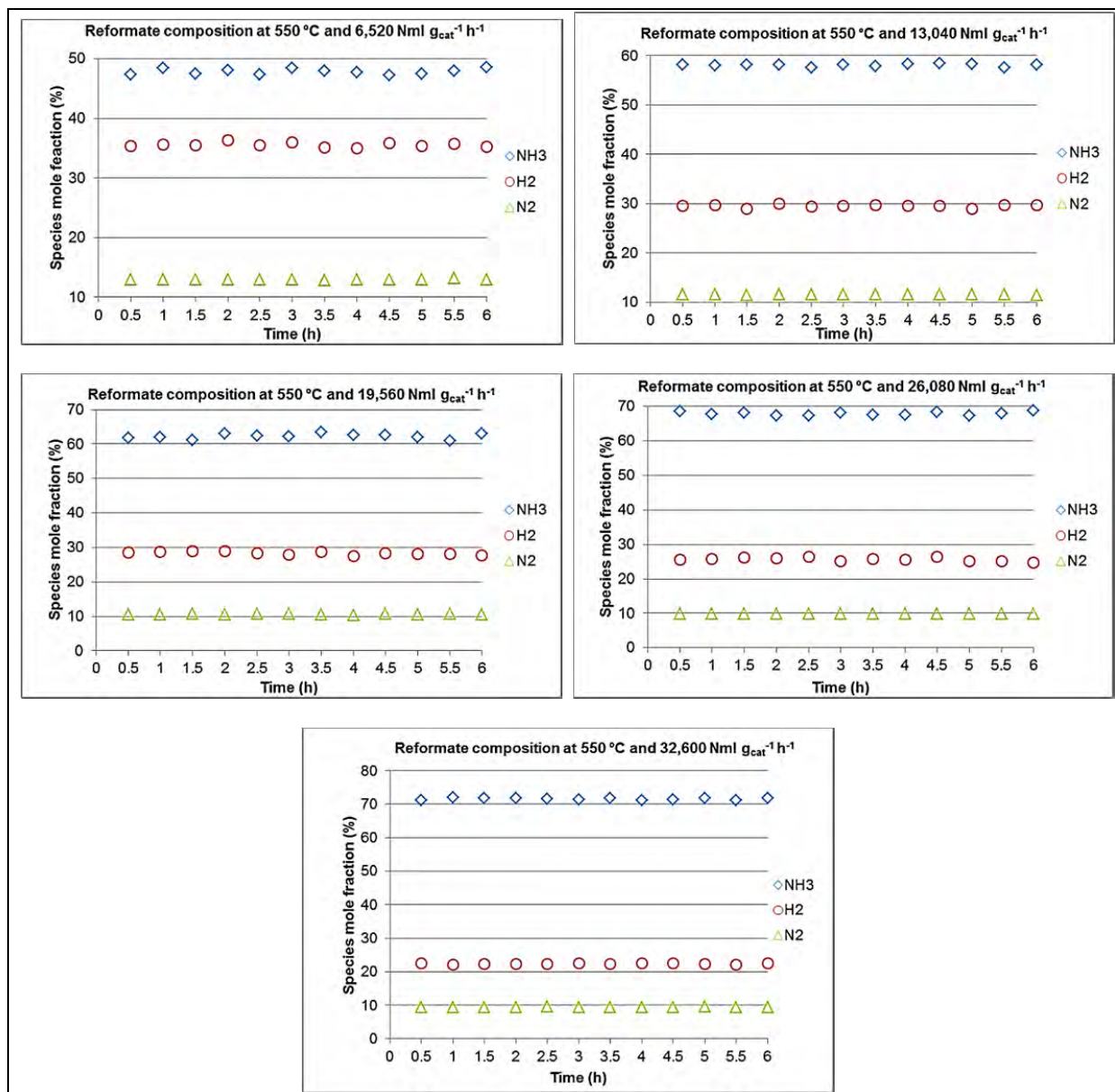


Fig. D-1 Species mole fraction profiles in reformat at 550 °C and GHSV = 6 520–32 600 Nml g_{cat}⁻¹ h⁻¹

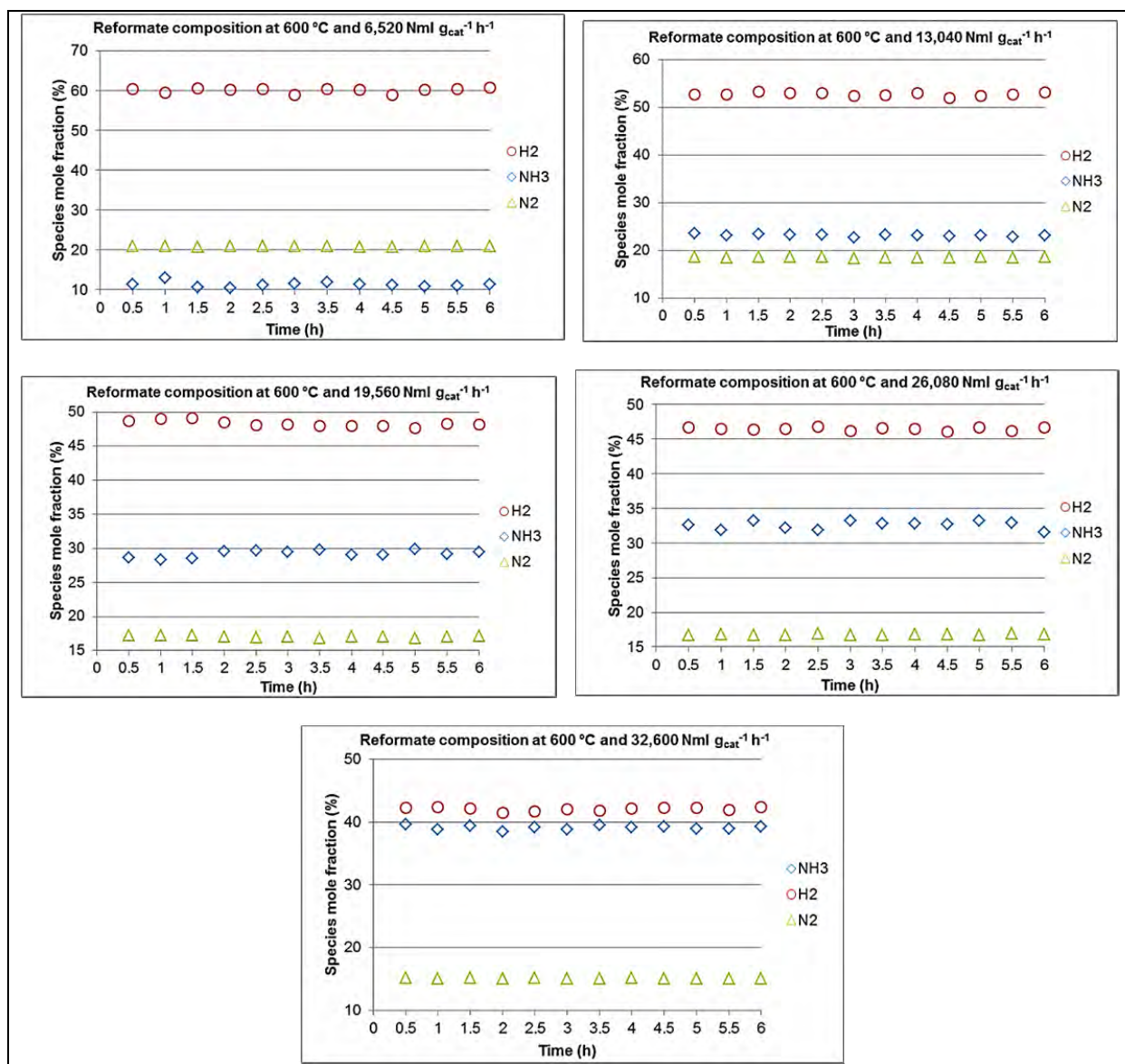


Fig. D-2 Species mole fraction profiles in reformat at 600 °C and GHSV = 6 520–32 600 Nml g_{cat}⁻¹ h⁻¹

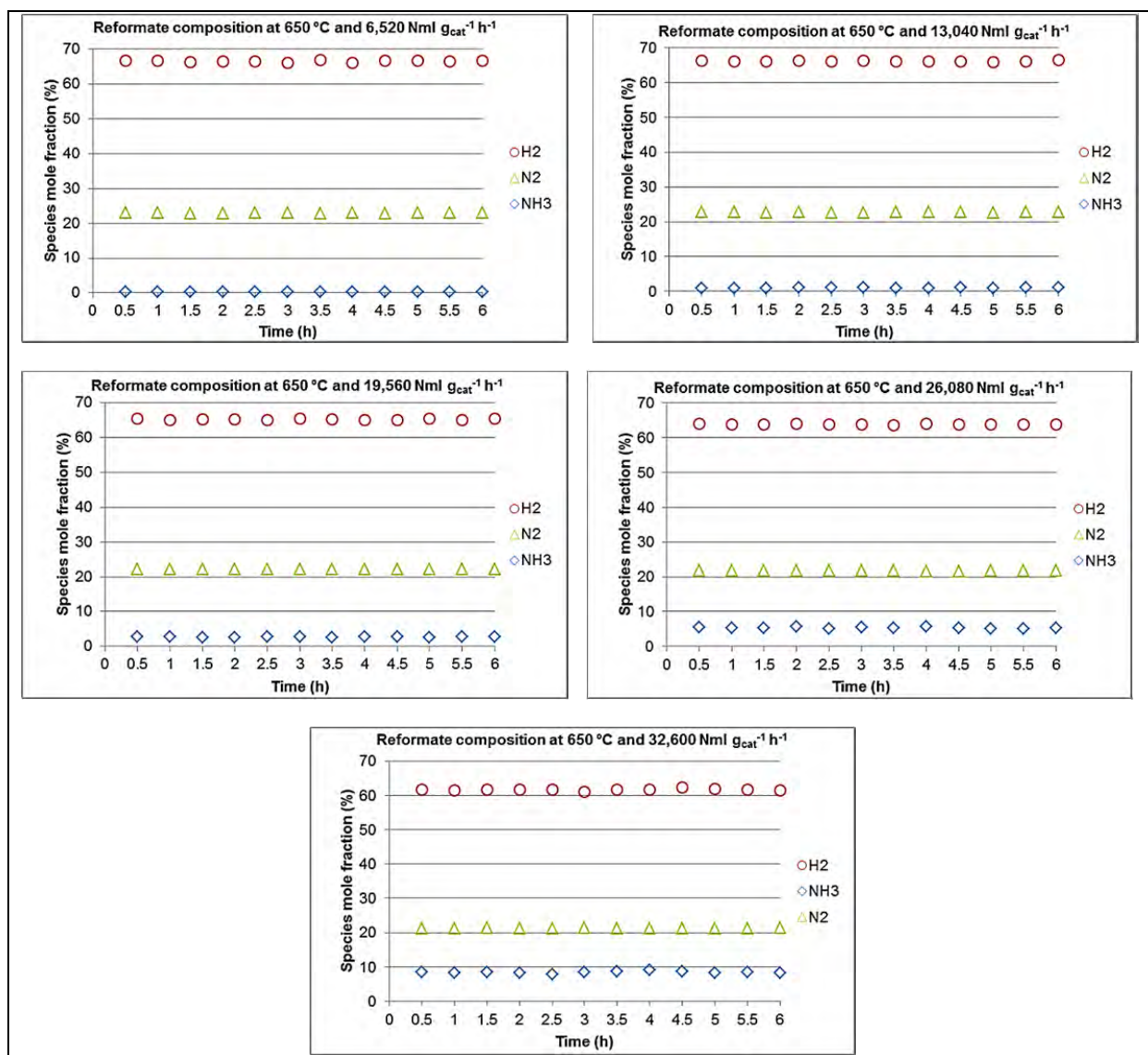


Fig. D-3 Species mole fraction profiles in reformat at 650 °C and GHSV = 6 520–32 600 Nml g_{cat}⁻¹ h⁻¹

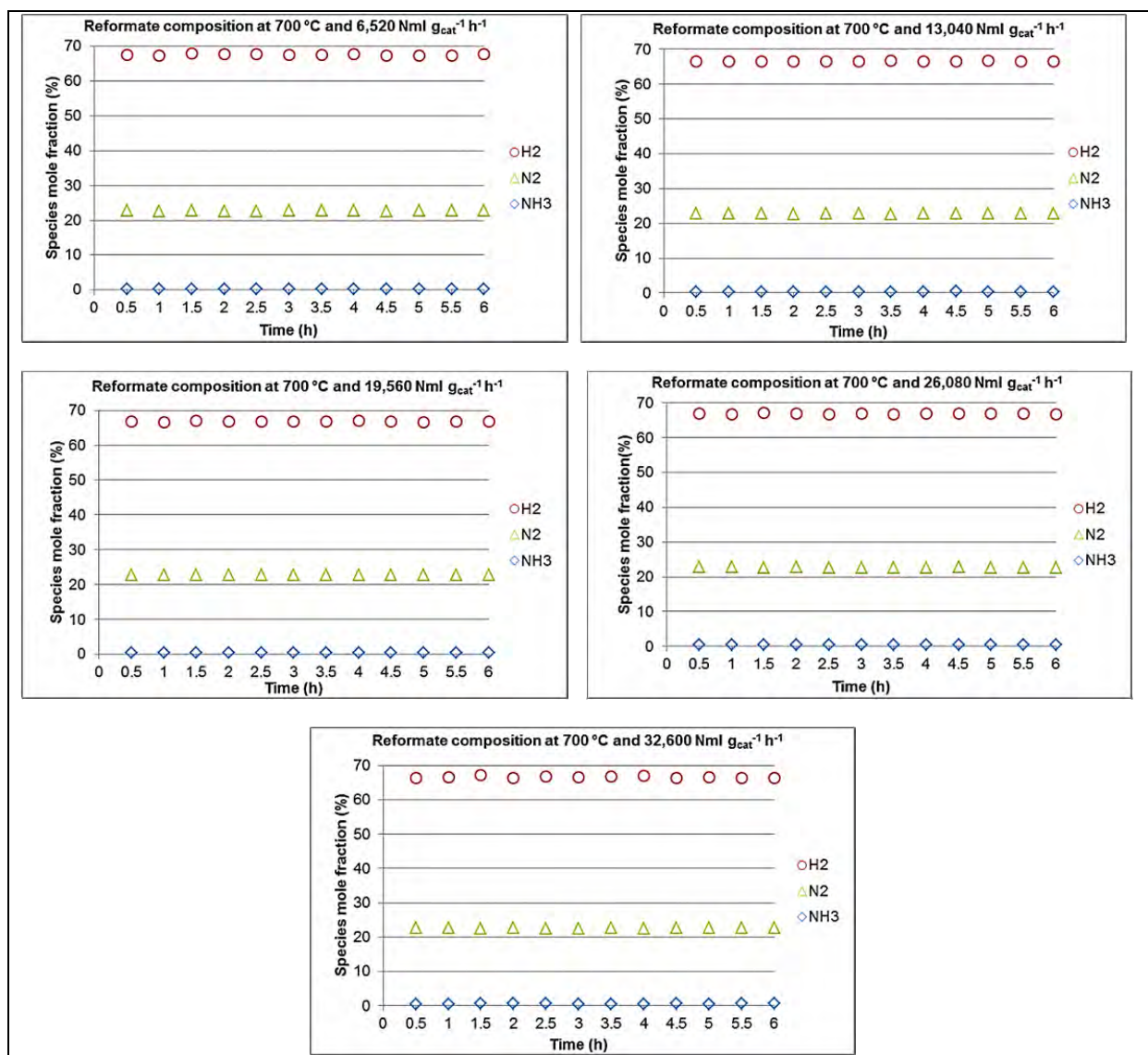


Fig. D-4 Species mole fraction profiles in reformat at 700 °C and GHSV = 6 520–32 600 Nml g_{cat}⁻¹ h⁻¹

APPENDIX E: REFORMATE GAS COMPOSITION Ru MICROREACTOR SYSTEM

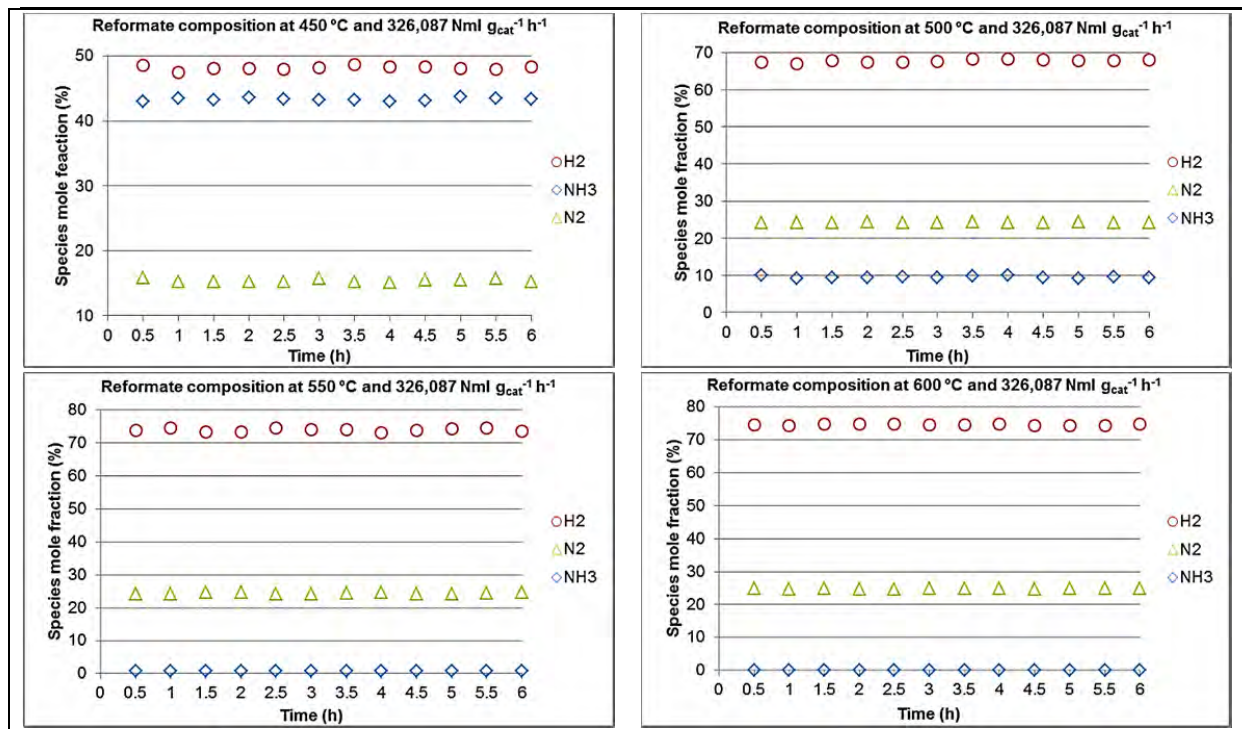


Fig. E-1 Species mole fraction profiles in reformat at GHSV = 326 087 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

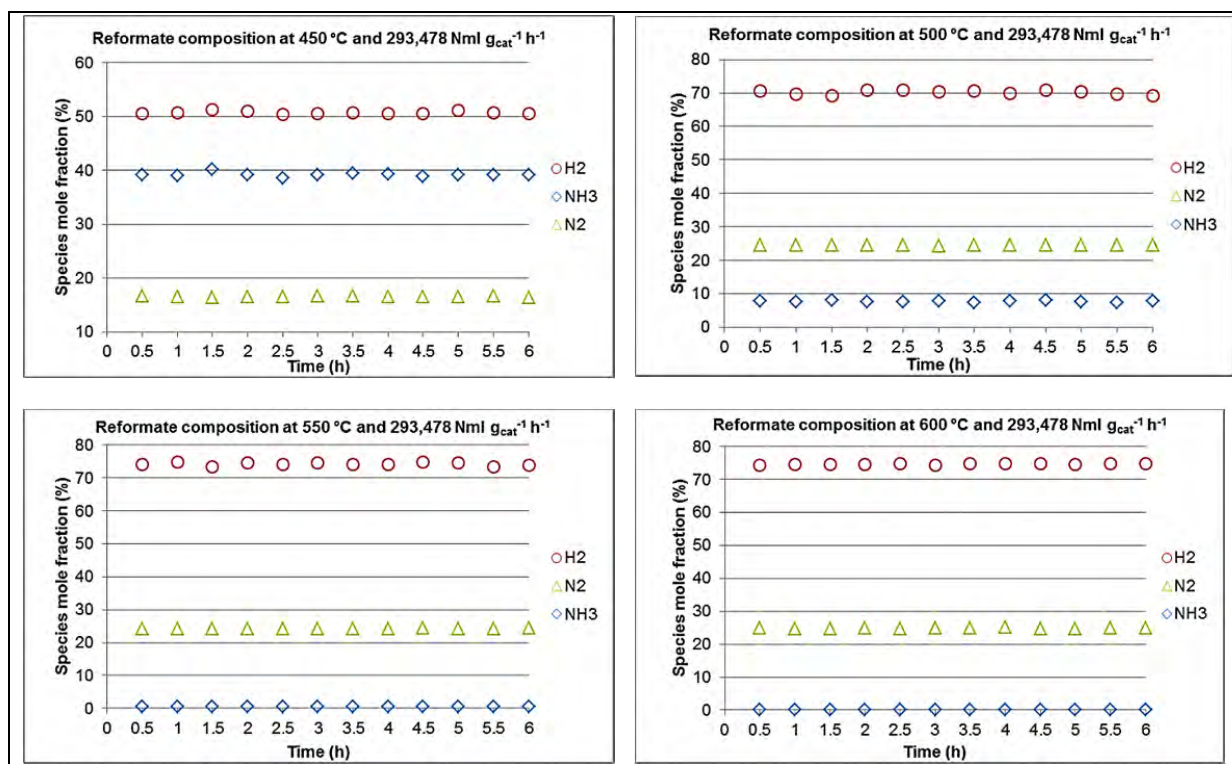


Fig. E-2 Species mole fraction profiles in reformat at GHSV = 293 478 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

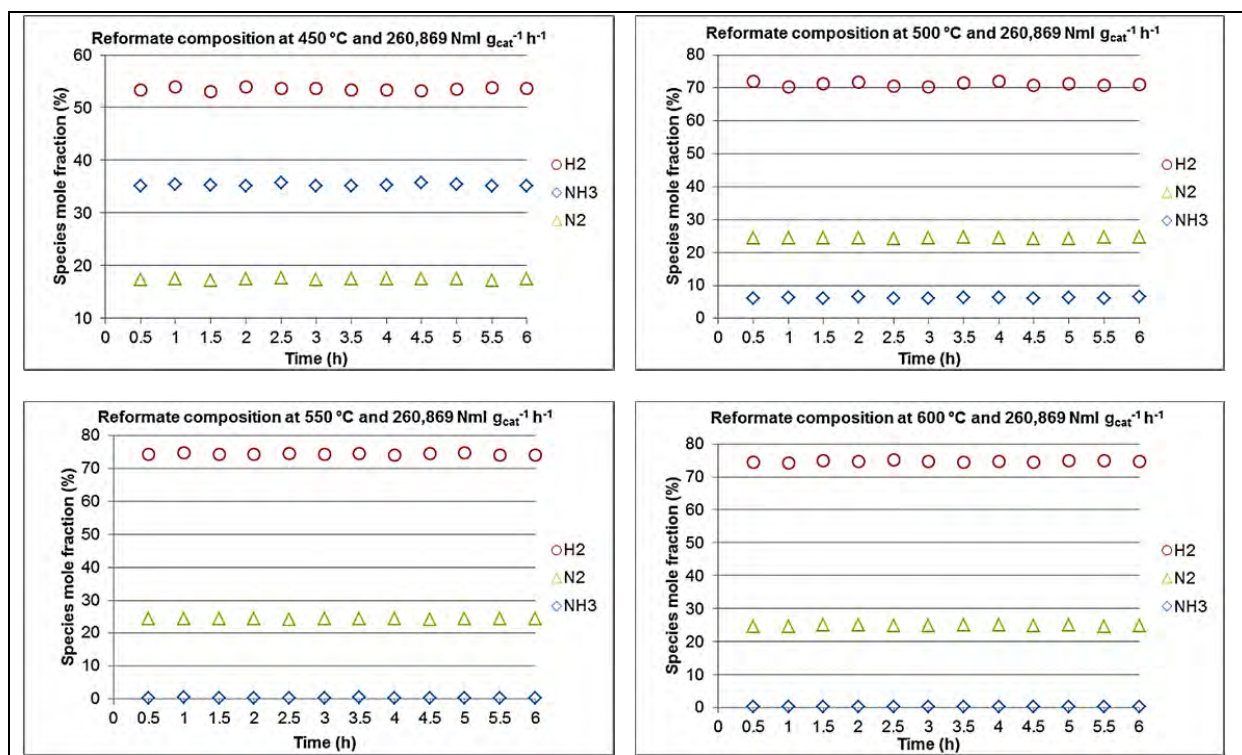


Fig. E-3 Species mole fraction profiles in reformat at GHSV = 260 869 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

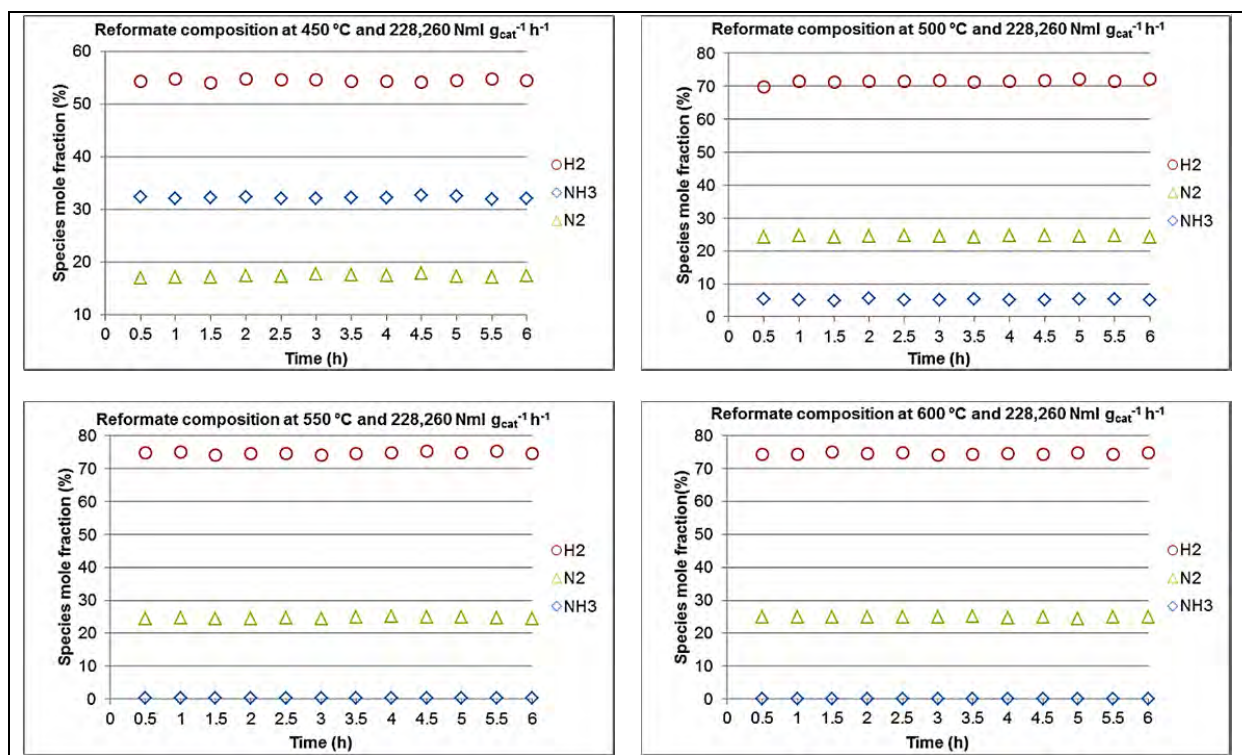


Fig. E-4 Species mole fraction profiles in reformat at GHSV = 228 260 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

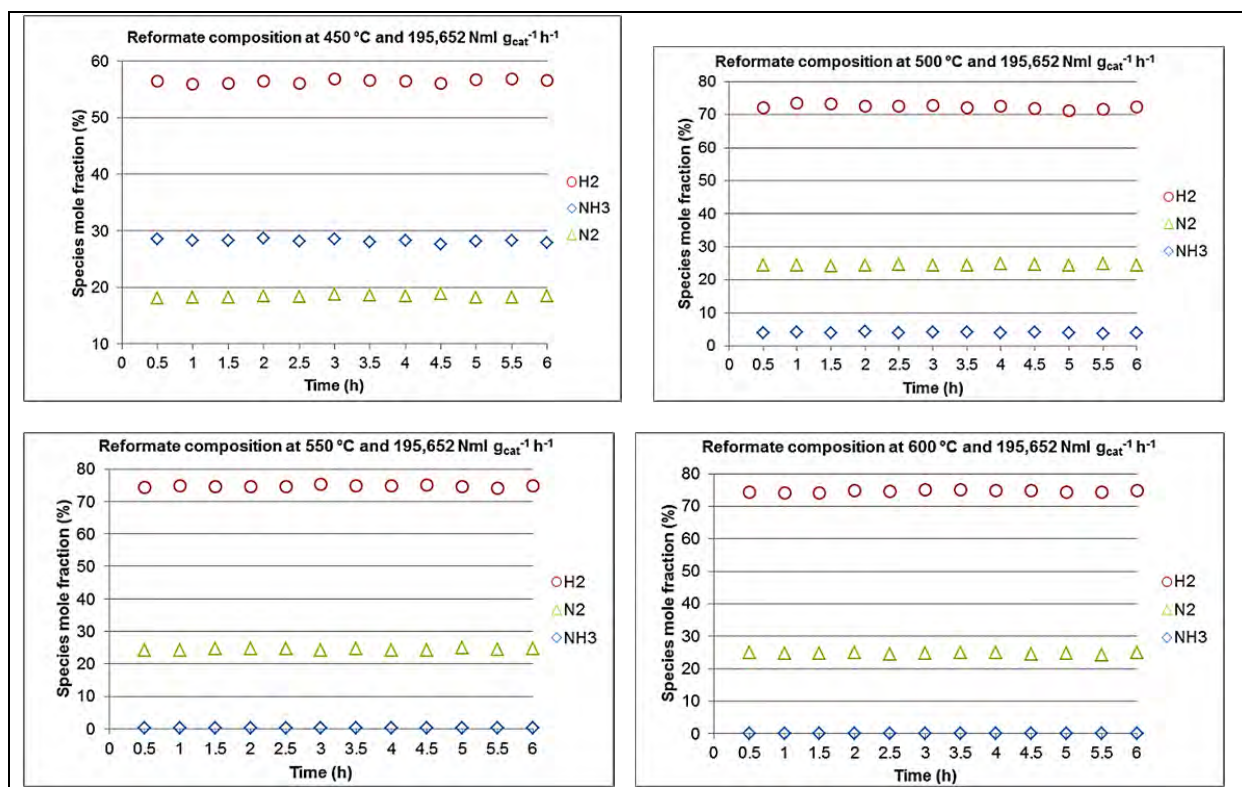


Fig. E-5 Species mole fraction profiles in reformat at GHSV = 195 652 Nml g_{cat}⁻¹ h⁻¹ and Tr = 450–600 °C.

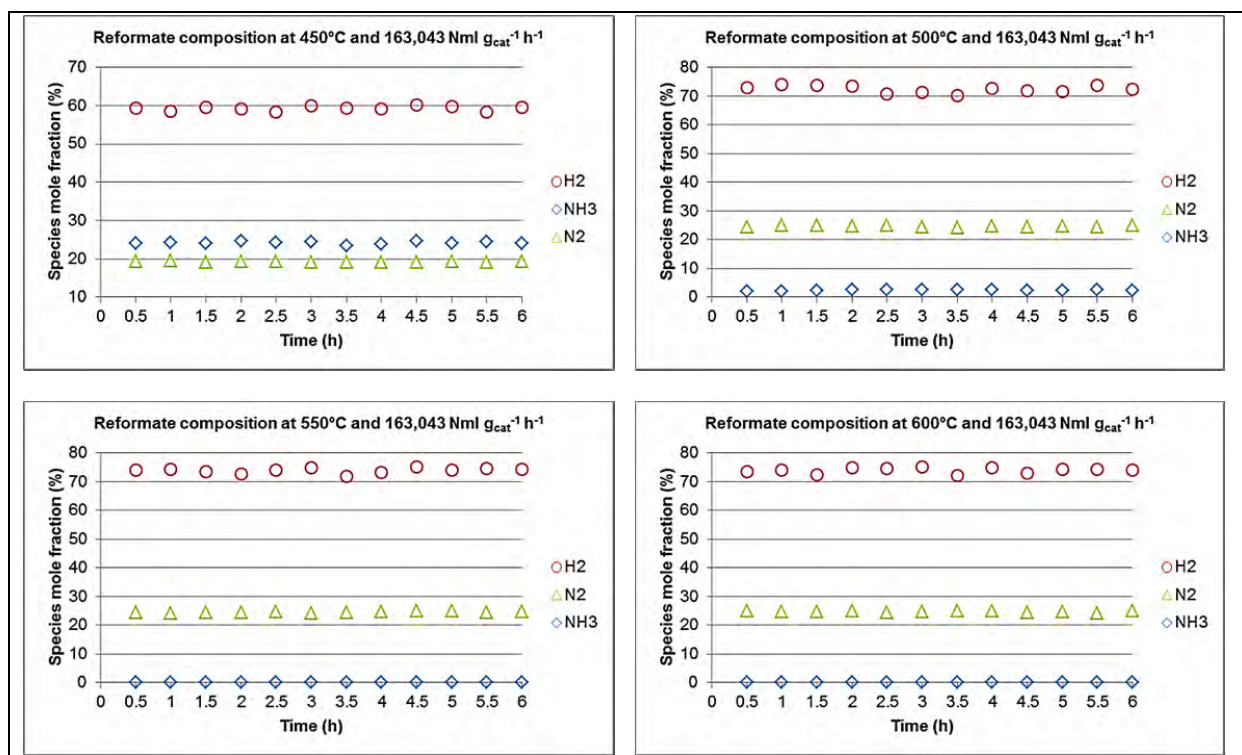


Fig. E-6 Species mole fraction profiles in reformat at GHSV = 163 043 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

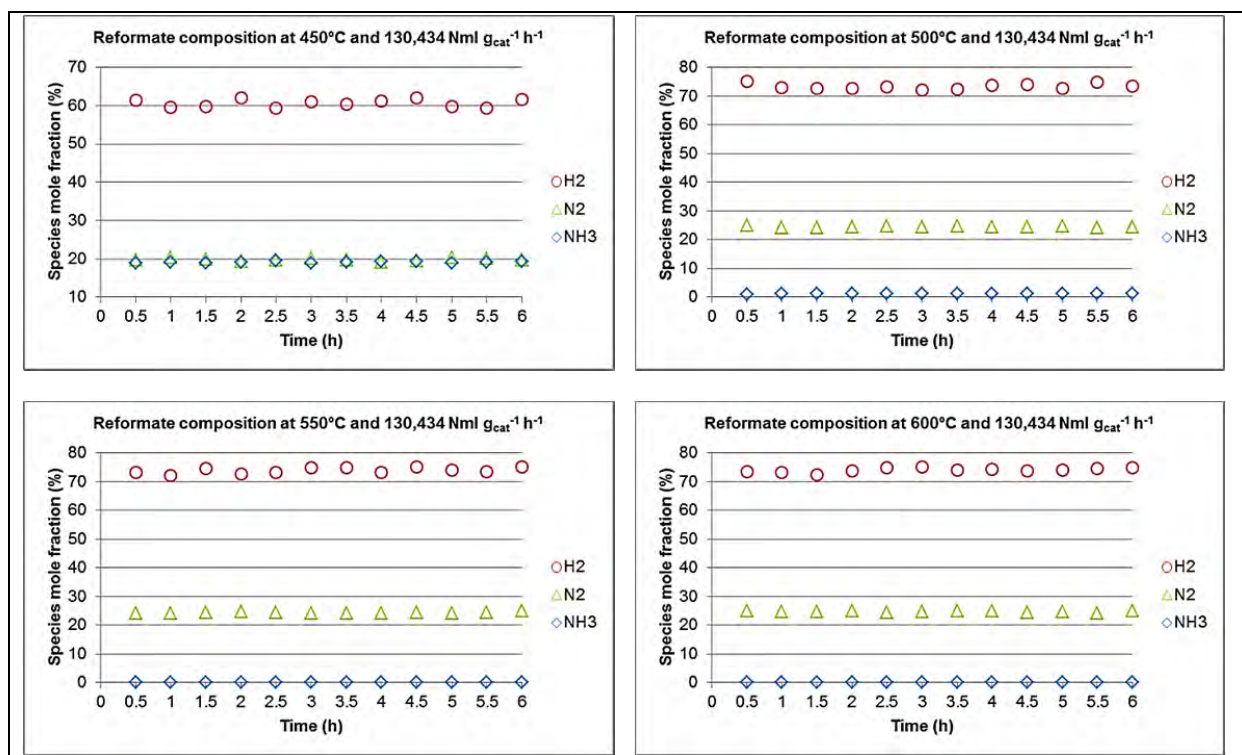


Fig. E-7 Species mole fraction profiles in reformat at GHSV = 130 434 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

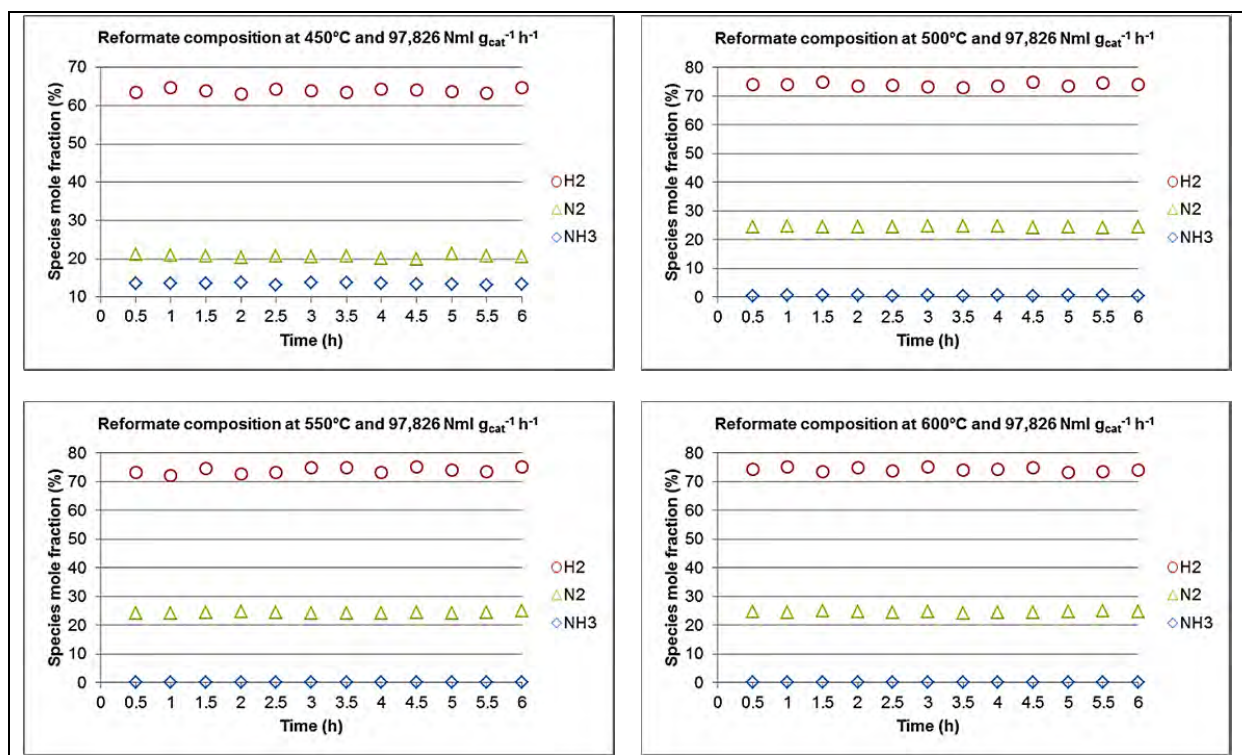


Fig. E-8 Species mole fraction profiles in reformat at GHSV = 97 826 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

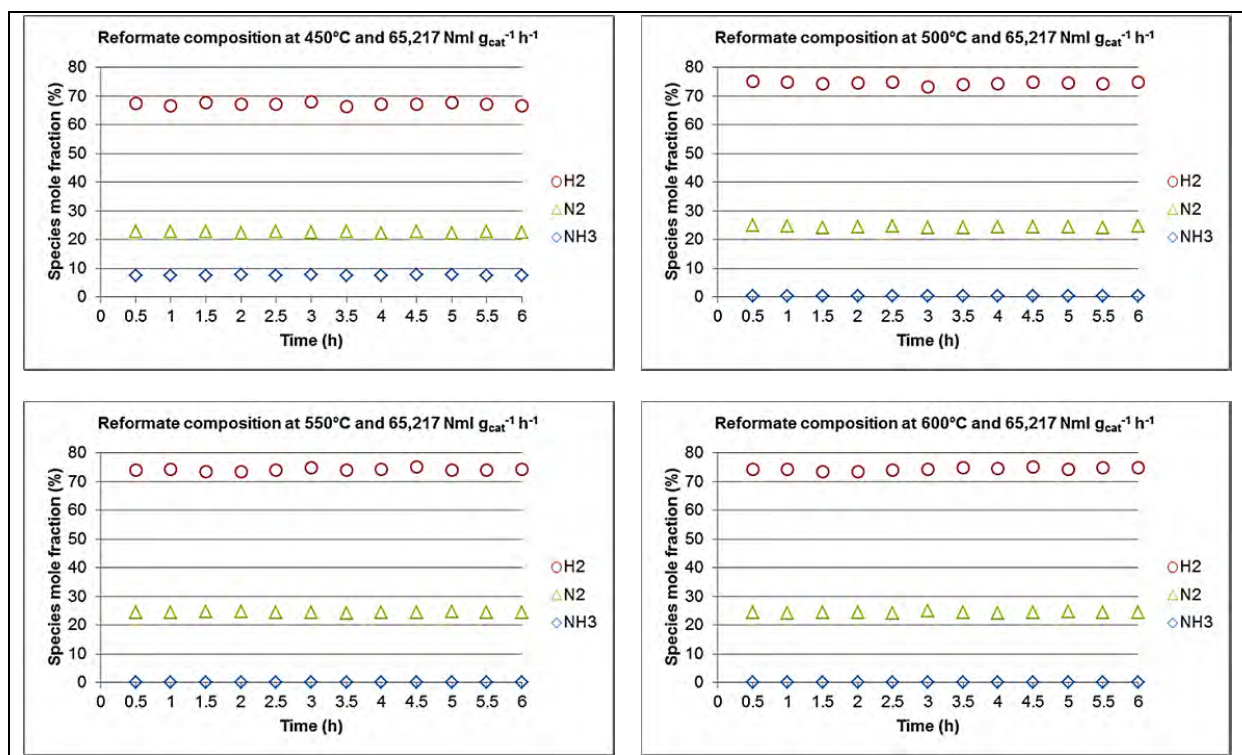


Fig. E-9 Species mole fraction profiles in reformat at GHSV = 65 217 Nml g_{cat}⁻¹ h⁻¹ and T_r = 450–600 °C.

APPENDIX F: SUPPLEMENTARY CFD MODELLING RESULTS

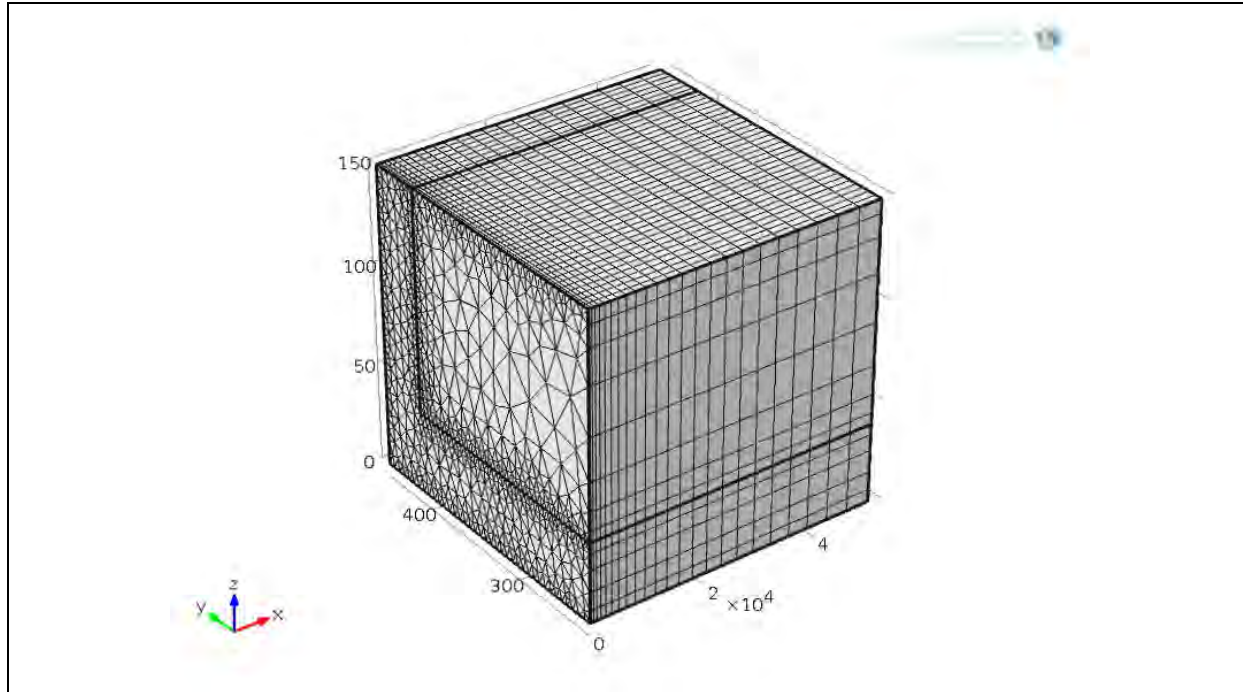


Fig. F-1 Computational mesh grid A (44 000 elements) for evaluating mesh-independent solution

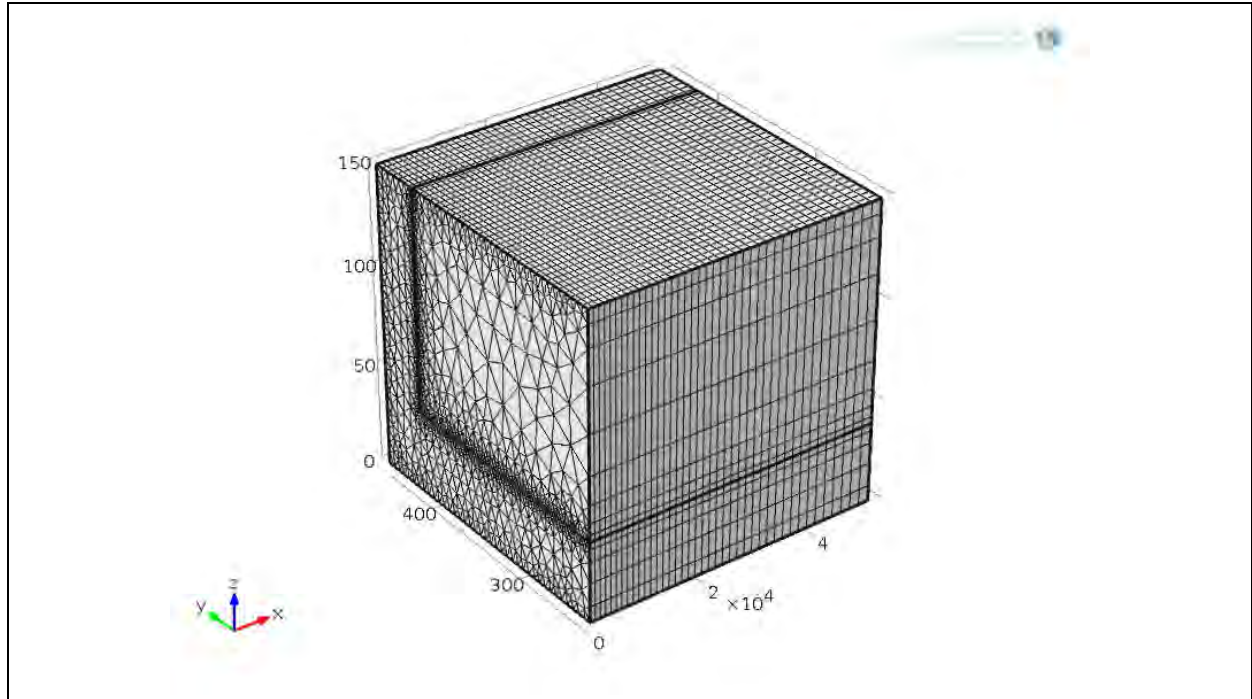


Fig. F-2 Computational mesh grid B (64 240 elements) for evaluating mesh-independent solution

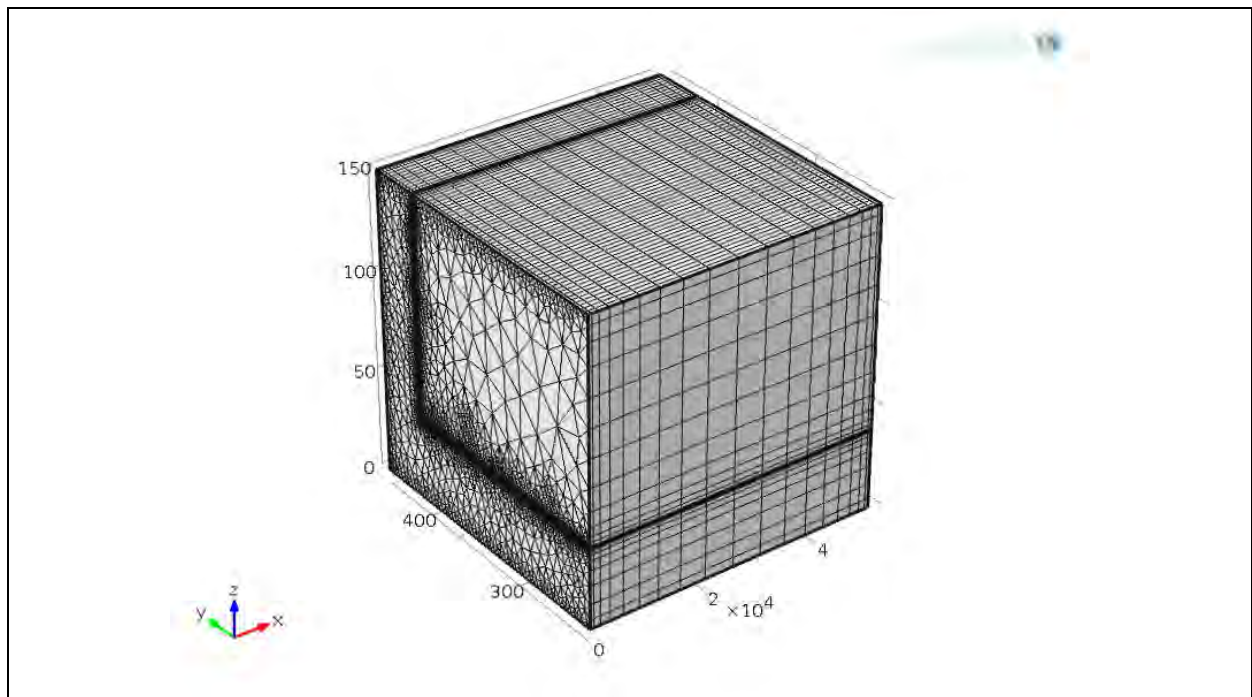


Fig. F-3 Computational mesh grid C (94 200 elements) for evaluating mesh-independent solution

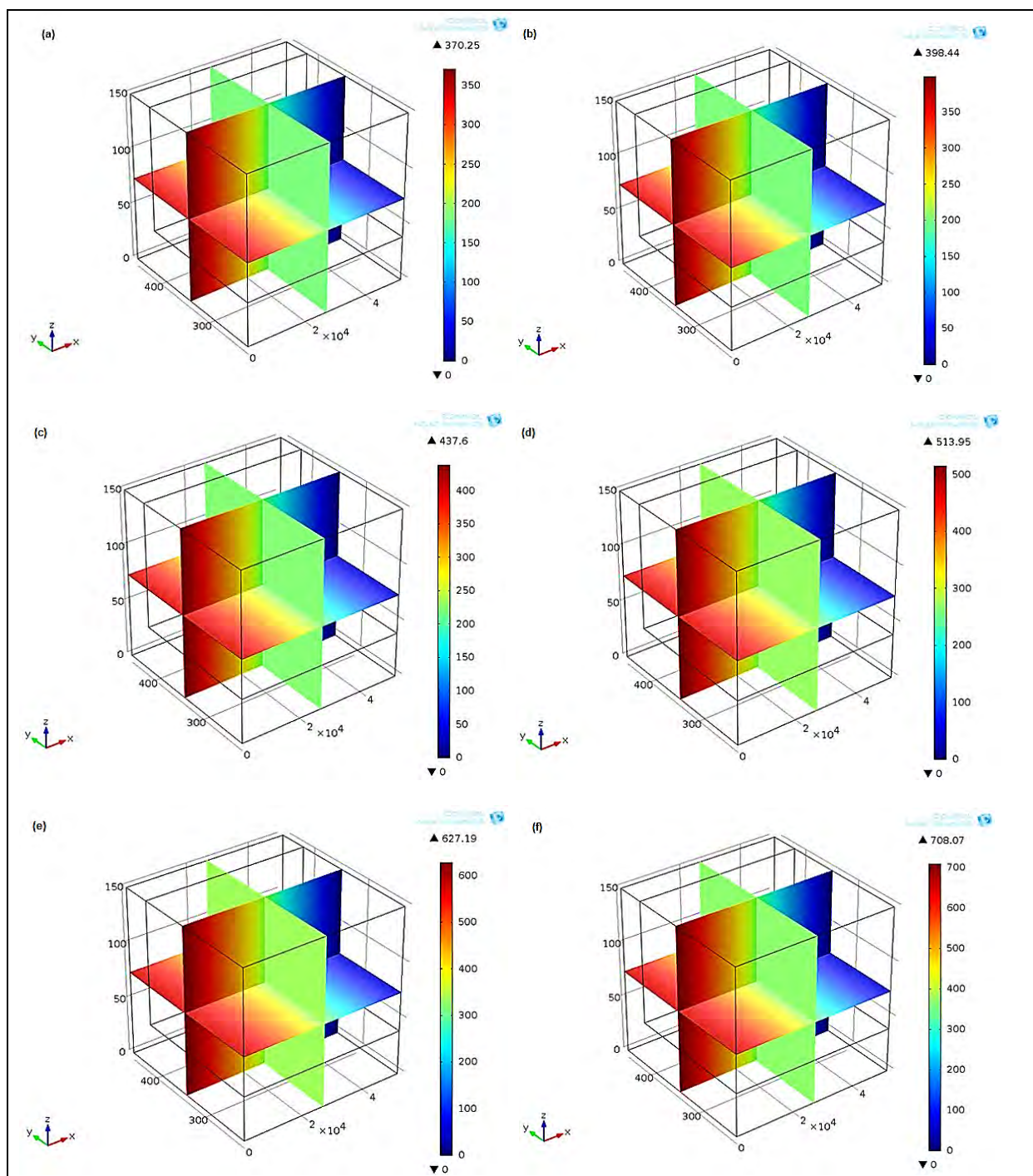


Fig. F-4 Pressure drop (Pa) profiles for baseline NH_3 flow rate (50 Nml min^{-1}) at different reactor temperatures (a) 723 K (b) 773 K (c) 823 K (d) 873 K (e) 923 K (f) 973 K

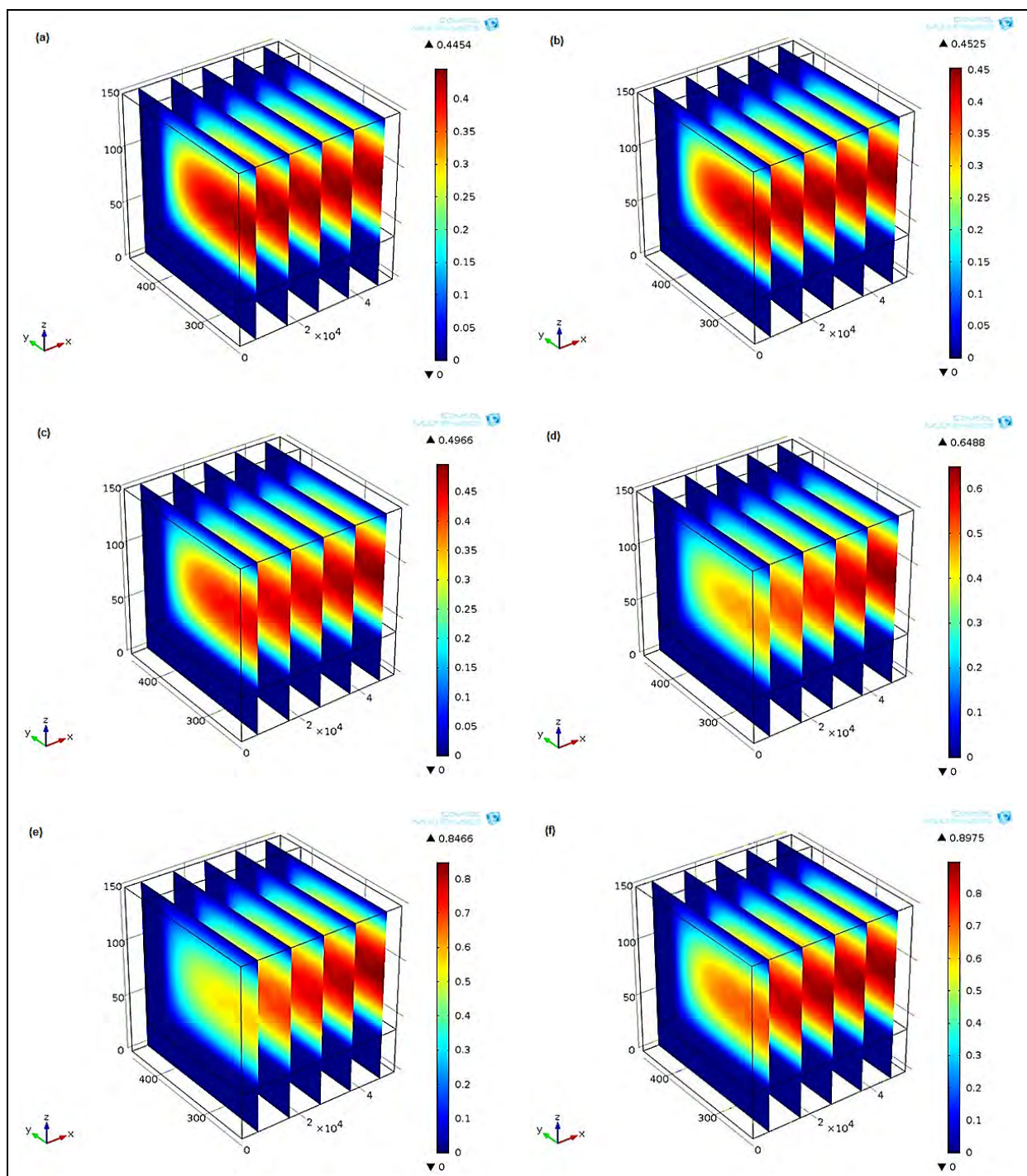


Fig. F-5 Velocity distributions (m s^{-1}) for baseline NH_3 flow rate (50 Nml min^{-1}) at different reactor temperatures (a) 723 K (b) 773 K (c) 823 K (d) 873 K (e) 923 K (f) 973 K

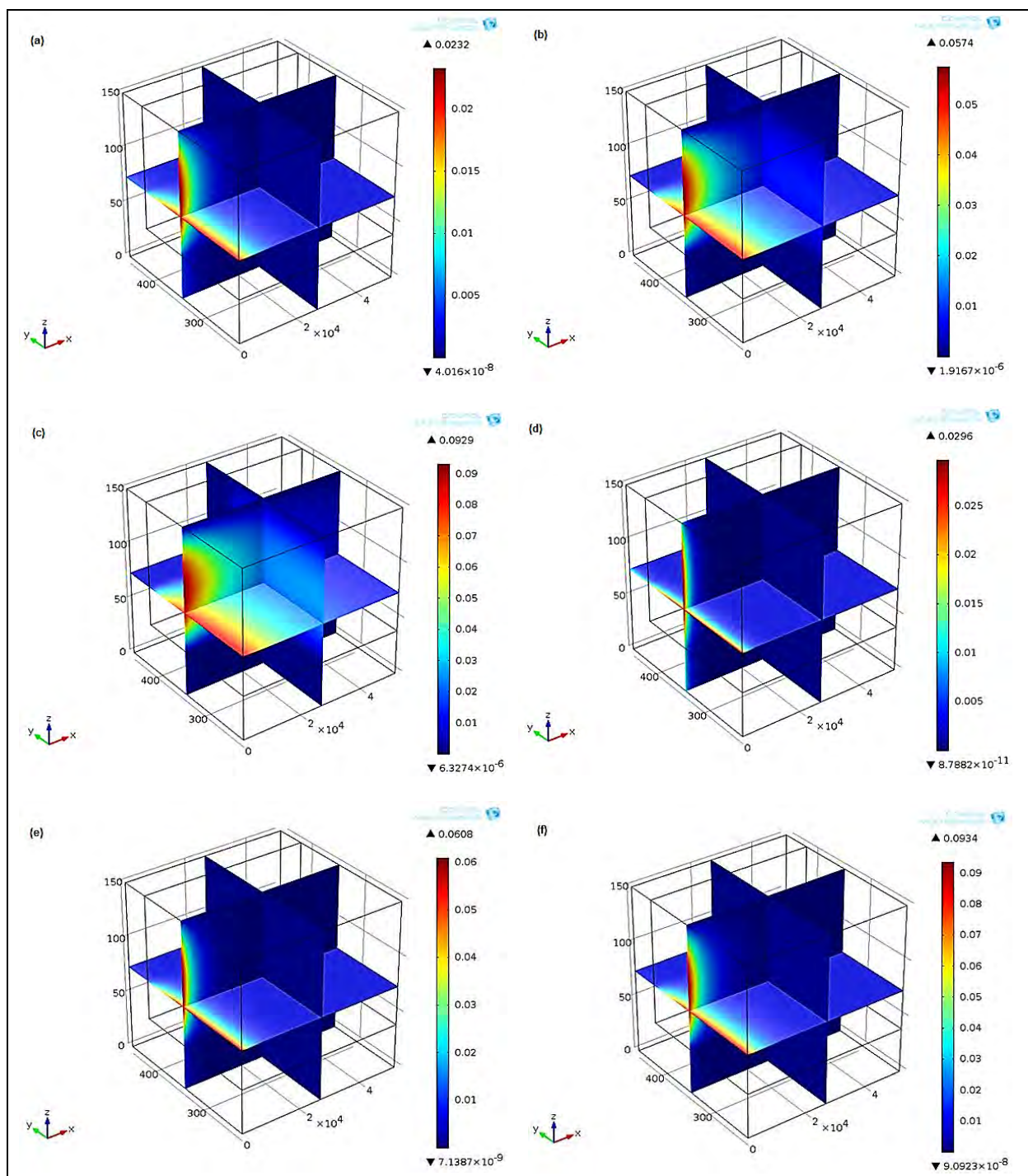


Fig. F-6 Total flux ($\text{kg m}^{-2} \text{s}^{-1}$) profiles for NH_3 at different combinations of NH_3 flow rate and reactor temperature (a) 10 Nml min^{-1} and 923 K (b) 30 Nml min^{-1} and 923 K (c) 50 Nml min^{-1} and 923 K (d) 10 Nml min^{-1} and 973 K (e) 30 Nml min^{-1} and 973 K (f) 50 Nml min^{-1} and 973 K

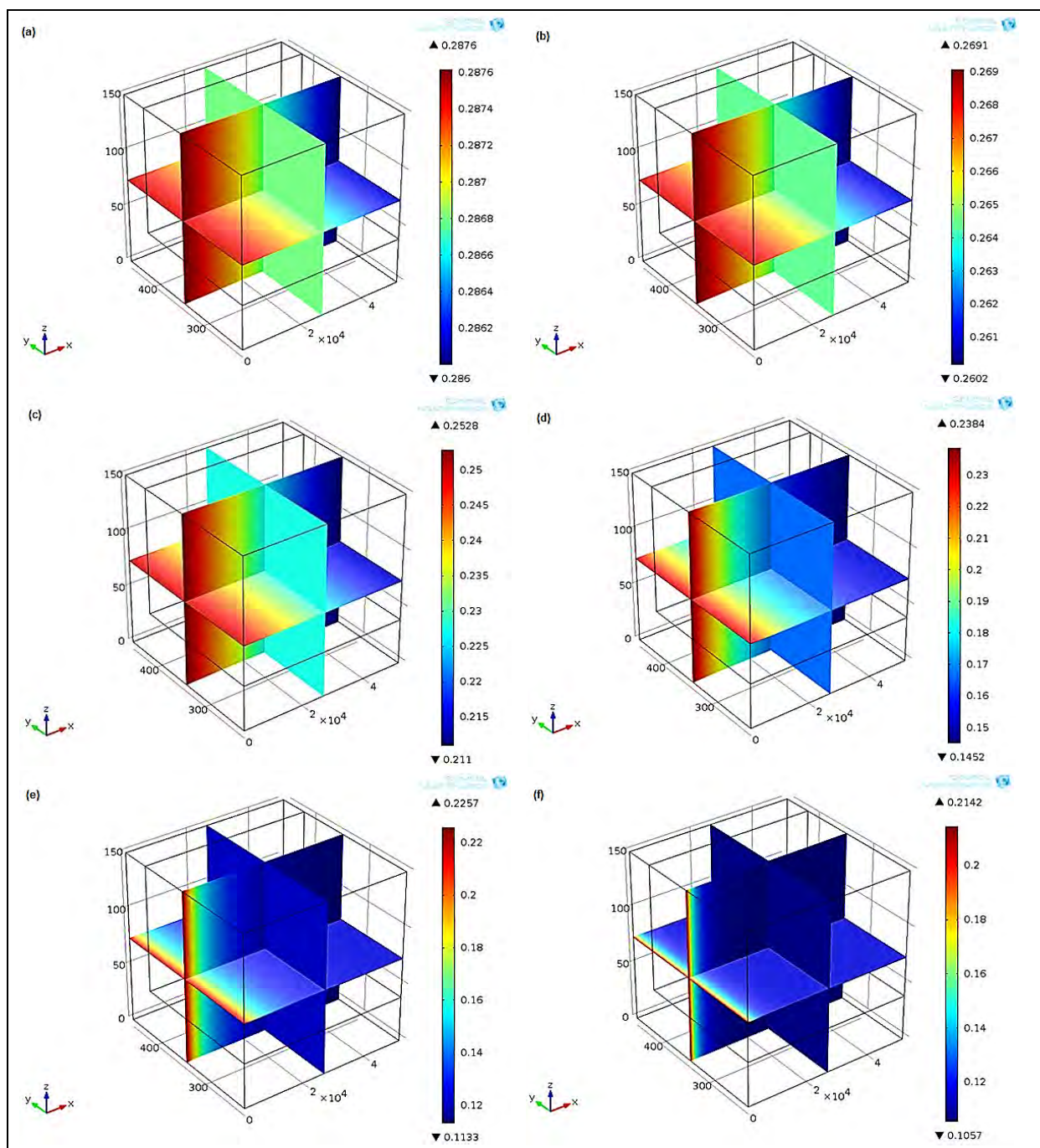


Fig. F-7 Overall gas density profiles within microchannel for $30 \text{ Nml min}^{-1} \text{ NH}_3$ flow rate at various reactor temperatures (a) 773 K (b) 773 K (c) 823 K (d) 873 K (e) 923 k (f) 973 K