



EXERGY ANALYSIS OF AN AMMONIA SYNTHESIS REACTOR IN A SOLAR THERMOCHEMICAL POWER SYSTEM

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Abstract—An ammonia-based thermochemical energy storage system is under investigation at the Australian National University. In recent years, one line of research has been the analysis of ammonia synthesis reactors. A two-dimensional numerical reactor model was previously validated with experimental results and was used in this study to compare maximum thermal output with maximum exergy output of the reactor investigated. The generic concept of exergy analysis is explained and some thermodynamic background is given. This study shows that a different set of ‘optimum’ reactor conditions results if optimized for maximum exergy output rather than maximum thermal output. Exergy analysis proved to be a useful technique for gathering information about the energy system investigated that would with an energy analysis purely based on first-law analysis not have been accomplished. Results tend to favour either very small diameter reactors to get close to the maximum rate curve or adiabatic reactors as used in industry.

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1. INTRODUCTION

A unique concept of thermochemically storing solar energy is under investigation at the Australian National University (ANU) and experimental as well as theoretical work have regularly been presented at ANZSES annual conferences (refer to, for example, Lovegrove, 1988; Luzzi, 1994; Luzzi *et al.*, 1997; Kreetz and Lovegrove, 1998; Lovegrove *et al.*, 1999a).

The concept as illustrated in Fig. 1 consists of a closed-loop system of reactants passing alternately to endothermic ‘solar’ and exothermic ‘heat recovery’ reactors. The reactors are connected via transport lines and a gas storage container. Counterflow heat exchangers, operated in conjunction with each reactor, ensure that storage and transport operate at ambient temperature. Synthesis and dissociation of ammonia ($\text{NH}_3 + \Delta H \rightleftharpoons 0.5 \text{N}_2 + 1.5 \text{H}_2$) offers advantages such as no side reactions and a large body of related industrial experience with ammonia synthesis. However, many different candidate reactions have been investigated since the 1970s, with carbon dioxide reforming of methane having received the most attention for solar application, in recent years (Levy *et al.*, 1993; Wörner and Tamme, 1998; Edwards *et al.*, 2000).

In recent years, one line of research at ANU has been the analysis of ammonia synthesis reactors. Lovegrove *et al.* (1999b) have carried out exergy efficiency studies of the exothermic half of the closed loop. A realistically achievable synthesis loop heat recovery exergy efficiency of 71% was found for a 30 MPa system resulting in an estimation of a solar-to-work conversion efficiency of around 20%. In an analysis of the $1 \text{ kW}_{\text{chem}}$ ammonia synthesis reactor used in the laboratory scale closed-loop system, experimental results were compared with the predictions of a numerical reactor model. The validity of the model was thus confirmed for ammonia synthesis (Kreetz and Lovegrove, 1999).

The industrial know-how of the ammonia synthesis industry is an important advantage for the solar thermochemical ammonia-based system. System components such as synthesis reactors or separators that are industry standard can be used in a first generation power plant. However, a solar ammonia power plant has different system optimization criteria. In particular, the exothermic ammonia synthesis reactor must be optimized for high temperature heat output in conjunction with electrical power generation rather than production rate of ammonia.

In this paper, the need for exergy or second-law analysis for evaluating a thermal power system and as a prerequisite for a thermo-economic (actually exergo-economic) optimisation is dis-

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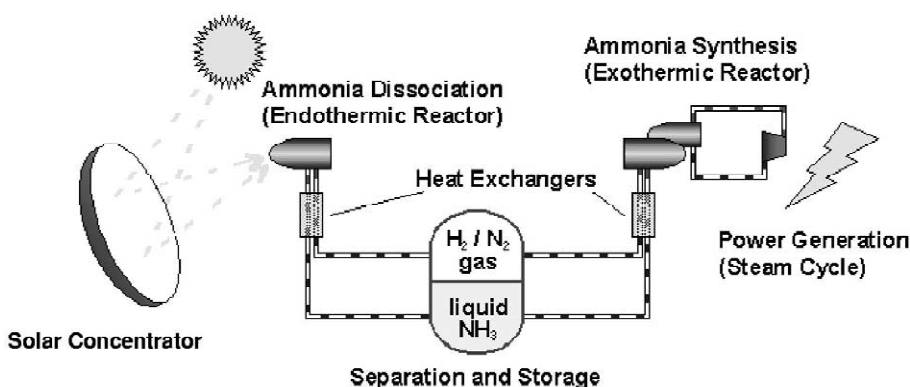


Fig. 1. Operation of closed-loop ammonia-based solar thermochemical energy storage system.

cussed. Some thermodynamic background of this concept is provided. An exergy analysis of the performance of the ANU ammonia synthesis reactor is then presented. The influence of reactor temperatures on the performance of the reactor is investigated for a wide pressure and temperature range. The correlation between maximum thermal and exergetic output is discussed. This work represents an important step towards a complete exergo-economic optimisation of the heat recovery half of the ammonia-based closed-loop system.

Consideration of exergy issues is timely, given the recently legislated requirement for 9500 GWh of new renewable electricity. Establishing the 'renewable electricity' contribution from hybrid solar/fossil systems, for example, cannot legitimately be based on energy analysis alone.

2. WHY EXERGY ANALYSIS?

Both the first and second law of thermodynamics determine effective use of energy resources when designing or improving energy systems. The first law — energy cannot be destroyed — is widely understood and energy system analysis today is mostly based on the first-law concept. However, an analysis based on the second law of thermodynamics quantifies the true value of various energy streams in terms of their potential for conversion to work (Bejan *et al.*, 1996). Such analysis can be based on the concept of exergy, in literature also referred to as 'availability' or 'available energy'.

In optimising the design of systems which aim to produce solar thermal electricity, it is readily apparent that exergy analysis has the potential to offer insights which are not available from first law analysis alone.

The second law concept can be embodied in a

convenient mathematical expression for an exergy balance for a control volume, i.e.

$$\frac{dE_{CV}}{dt} = \sum_j \left(1 - \frac{T_o}{T_j} \right) \cdot \dot{Q}_j - \left(\dot{W}_{CV} - p_o \cdot \frac{dV_{CV}}{dt} \right) + \sum_{in} \dot{m}_{in} \cdot e_{in} - \sum_{ex} \dot{m}_{ex} \cdot e_{ex} - \dot{E}_D \quad (1)$$

where dE_{CV}/dt is the time rate of exergy change. $\sum_j (1 - T_o/T_j) \cdot \dot{Q}_j$ represents the rate of exergy transfer associated with heat transfer \dot{Q}_j at a boundary with the temperature T_j as derived with Carnot's principle. $\dot{W}_{CV} - p_o \cdot dV_{CV}/dt$ is the rate of exergy transfer associated with work where dV_{CV}/dt is the rate of change of system volume. $\dot{m}_{in} \cdot e_{in}$ and $\dot{m}_{ex} \cdot e_{ex}$ account for the rate of exergy transfer associated with massflows. \dot{E}_D accounts for the exergy destruction due to irreversibilities within the control volume.

The concept of exergy is extensively discussed in the books of Kotas (1995), Szargut *et al.* (1988) and Barclay (1998). The concept of exergoeconomics where exergy analysis is combined with economic considerations to provide the plant designer with crucial information to the design and operation of a cost-optimized plant is presented by Tsatsaronis (1996) and Bejan *et al.* (1996). The Laboratory of Thermal Engineering at the University of Twente provides thermodynamic background and a good literature review on the basic concept of exergy (<http://www.thw.wb.utwente.nl/topics/exergy.htm>).

3. AMMONIA SYNTHESIS REACTOR STUDY

Industrial experience of the ammonia synthesis industry is a major advantage of the ammonia system. The 'Haber–Bosch' process for catalytic synthesis of ammonia was developed nearly 100

years ago. According to Appl (1999) in a review of the industry, ammonia synthesis 'is probably the most investigated heterogeneous catalytic reaction of all'.

In recent years, most converters have been designed with catalyst distributed in several beds, with the gases reacting under close to adiabatic conditions. Detailed reviews of recent developments are given by Dybkjaer (1995), Appl (1999) and Ullmann's (1996). The main distinguishing characteristic of different designs, is the approach taken to remove the energy released by the exothermic reaction and thus to control the operating temperature of the catalyst beds. Modern units have heat exchangers suitable for the production of superheated steam for power generation included. However, while such units could be used in a first generation power plant, it is worth investigating whether changes in the method of heat recovery could improve overall system performance.

3.1. Modelling experimental reactors

The performance of tubular packed-bed catalytic ammonia reactors has been predicted with a two-dimensional pseudo-homogeneous model. The original version of this Fortran program was developed by Richardson *et al.* (1988) for tubular packed-bed steam/methane-reforming reactors and has been modified and validated for ammonia dissociation via extensive experiments using an electrically heated 1 kW_{chem} ammonia dissociator (Lovegrove, 1996). To model the behaviour of the reactor, simultaneous reaction, heat and mass transfer mechanisms have to be taken into consideration. A specification of an arbitrary temperature profile, flux profile or heat transfer fluid is needed as the reactor wall boundary condition.

A laboratory-scale ammonia synthesis reactor has been investigated experimentally in a closed-loop energy storage system operation. This work has enabled the validity of the numerical model to be confirmed for ammonia synthesis. A detailed description of the construction and the experimental arrangement used has been presented by Kreetz and Lovegrove (1999). The 1005 mm long, 21.3 mm o.d., 15.8 mm i.d. ammonia synthesis reactor has been operated at pressures between 9.3 and 19 MPa, massflows around 0.3 g s⁻¹ and temperatures up to 524°C.

For the investigation presented here, linear temperature profiles were assumed as the reactor wall boundary condition. The Fortran code has been incorporated in a Matlab program to accelerate the process of multiple simulation runs for

parameter variations. It calculates the rate of heat and exergy recovery from the reactor with the results of the Fortran program and writes simulation result data in output files systematically. Enthalpy and Gibbs' free energy values used in this study were calculated with thermodynamic data that have been established for ammonia/hydrogen/nitrogen mixtures by Williams (1978) and prepared and extended for direct use with modelling by Lovegrove (1992).

3.2. Exergy analysis of tubular reactors

The exergy analysis carried out in this paper is based on the design of the laboratory-scale ammonia synthesis reactor previously investigated experimentally. Fig. 2 shows the system studied, divided up into subsystems containing the reactor and a preheater. Note that a 'real' system may contain an internal preheater in which a counter flowing heat recovery fluid extracts heat from the catalyst bed of the reactor, this study assumes loss free and external preheating with

$$\dot{E}_{\text{preheat}} = \dot{m} \cdot (h_2 - h_1 - T_o \cdot (s_2 - s_1)) \quad (2)$$

where \dot{E}_{preheat} represents the time rate of exergy transfer by work and s_i are the specific entropies at the specific locations indicated. Since thermodynamic data were available as tables of Gibbs' free energy and enthalpies, entropies were calculated using

$$s_i = \frac{h_i - g_i}{T_i} \quad (3)$$

The gas inlet temperature of the preheater was assumed to be equal to the reactor wall exit temperature ($T_1 = T_{3w}$) as could be the case in a real internal preheating system. The net exergy rate is maximised in this study which is, in other

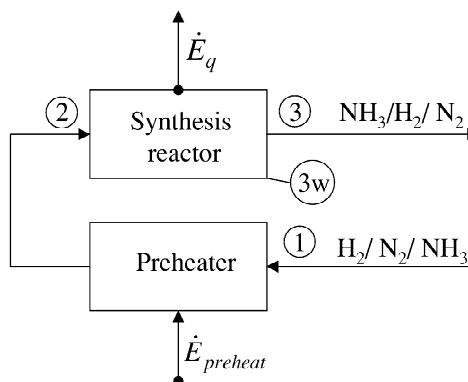


Fig. 2. Subsystems used in exergy analysis of tubular ammonia synthesis reactor.

Table 1. Simulation runs: range of parameters

Parameter	Range of operation
Reactant flow rate	0.1 to 1.1 g s ⁻¹
Pressure	10 to 30 MPa
Reactor inlet gas temperature	300 to 700°C
Outer reactor wall temperature at start of bed	300 to 700°C
Slope of linear outer reactor wall temperature profile	−4 to 2°C cm ⁻¹

words, the exergy provided by the exothermic reaction less the exergy needed to preheat the reactants. This is mathematically described by

$$\dot{E}_{\text{net}} = \dot{E}_q - \dot{E}_{\text{preheat}} \quad (4)$$

where

$$\dot{E}_q = \sum_j \dot{Q}_j \cdot \left(1 - \frac{T_o}{T_j}\right) \quad (5)$$

is the rate of exergy transfer associated with the heat transfer at the rate \dot{Q}_j . T_j represents the average outer reactor wall temperature at each increment, T_o was assumed to be 300 K. In this study, an exergy analysis of the reactor plus preheater was carried out and compared to previous studies which examined thermal output maximisation¹ of the reactor (Kreetz *et al.*, 2000). The influence of the preceding counter-flow heat exchanger (refer to Fig. 1) was not investigated here. Although, it will be an important part for a complete system optimisation.

Variation of flow rate, pressure, inlet gas temperature and reactor wall temperatures was investigated. Table 1 shows the range of parameters used.

A fixed value of 0.98 was used for the inlet reaction extent² as it reflects a typical experimental value. The maximum massflow investigated was 1.1 g s⁻¹, representing a typical maximum experimental value. For each massflow–pressure combination investigated, maximum thermal and net exergy rate were found by modelling the reactor with a range of gas inlet temperatures, and linear wall temperature profiles given by:

$$T_z = T_{2w} + b \cdot z \quad (6)$$

where T_z (°C) is the internal reactor wall tempera-

ture at location z , T_{2w} (°C) is the outer reactor wall temperature at location 2, b (°C cm⁻¹) is the slope of the linear temperature profile and z (cm) is the distance from the beginning of the bed.

3.2.1. Features of maximum thermal and ex-ergetic output reactor profiles. The temperature and reaction extent profiles of all optimum configurations were found to share a number of common features for maximising heat recovery or net exergy output, respectively. Fig. 3 (for max. heat recovery) and Fig. 4 (for max. net exergy rate) show modelled average internal and external reactor temperature profiles plus the corresponding reaction extent profiles for three representative massflow/pressure combinations. The horizontal axis shows position along the catalyst bed as measured from the point of gas inlet. In the bottom graphs of both Figs. 3 and 4, the equilibrium line indicates the calculated equilibrium composition corresponding to the average internal reactor temperature at each position at the given pressure. Since ‘plug flow’ is assumed in the model, these average values are area weighted averages across the catalyst bed at each point.

In case of the maximum heat recovery profiles, maximum output is achieved with a constant ‘distance’ between the average composition within the reactor and the thermodynamic equilibrium composition corresponding to the average temperature within it. This apparent ‘constant distance from equilibrium’ rule, determines the best gas inlet temperature for a given composition at inlet and the best initial wall temperature and rate of decrease in wall temperature along the bed.

This behaviour reflects the effect of reactor conditions on reaction rates. In general terms, higher temperatures work to increase reaction rates whilst an approach to chemical equilibrium conditions works to reduce them. Thus, maximum output will be achieved by keeping the average temperature in the reactor as high as possible without getting too close to equilibrium. This means that as more ammonia is produced along the length of the reactor, average temperatures need to fall to maintain the necessary ‘distance’

¹Net thermal power output was calculated from the enthalpy change of reactants assuming they start and finish at 300 K. Maximum thermal power output was achieved for maximum change of reaction extent, with the amount of energy released proportional to the massflow and the enthalpy of the reaction (66.8 kJ mol⁻¹ ammonia at 20 MPa, 300 K).

²Reaction extent is defined as the mass fraction of 3:1 hydrogen/nitrogen in a gas mixture.

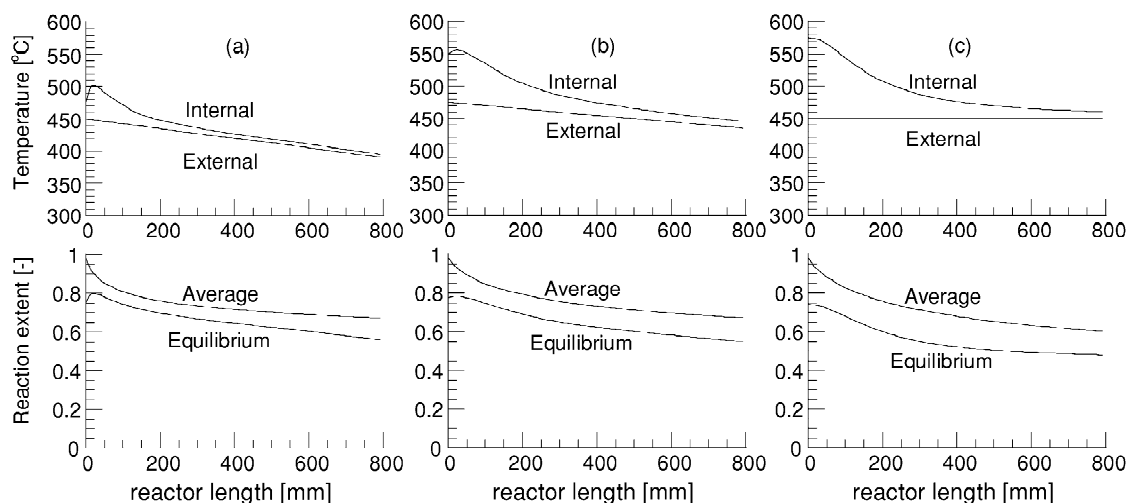


Fig. 3. Representative modelled average internal and external reactor temperature profiles plus the corresponding reaction extent profiles for the optimum recovery of heat for three different massflows and pressures (a, 10 MPa, 0.1 g s⁻¹; b, 20 MPa, 0.7 g s⁻¹; c, 30 MPa, 1.1 g s⁻¹).

from equilibrium. If the reactor was of infinitesimal diameter then for each point along its length, the composition would determine a single temperature which would produce the maximum reaction rate. However, for a reactor of finite diameter a radial temperature gradient is needed to support the necessary heat transfer to the wall. In these circumstances the optimum temperature distribution in the reactor will be a compromise between maximising rates at each point whilst maintaining the heat transfer. The initial increase in internal temperatures indicated in Fig. 3a reflects the combination of these effects together with the boundary condition assumed by the

model, of radially uniform initial temperatures equal to the gas inlet temperature.

In determining the maximum net exergy output, there are three influences that must be traded off. Increasing thermal output also works to increase exergy output. Operating the reactor at higher temperatures than suggested for maximum thermal output although reducing thermal output, increases the average theoretical conversion efficiency. Finally, increasing the gas inlet temperature to improve reactor output, carries the penalty of requiring increased exergy input for pre-heating, which is partially destroyed due to heat transfer limitations in the reactor.

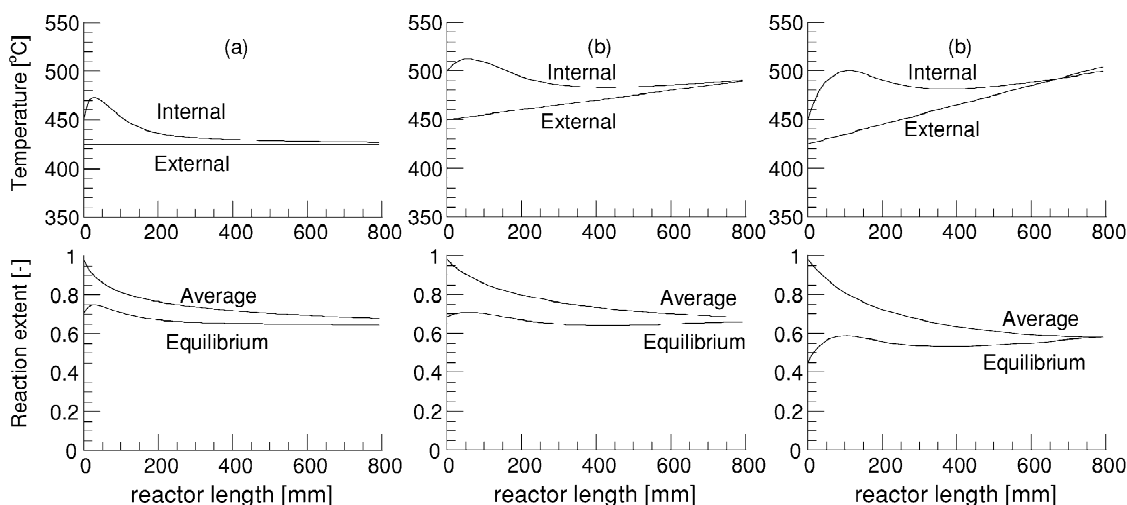


Fig. 4. Representative modelled average internal and external reactor temperature profiles plus the corresponding reaction extent profiles for the maximum net exergy rate for three different massflows and pressures (a, 10 MPa, 0.1 g s⁻¹; b, 20 MPa, 0.7 g s⁻¹; c, 30 MPa, 1.1 g s⁻¹).

In case of maximum net exergy rate, Fig. 4, maximum output is achieved with the internal average composition being close to equilibrium at the end of the bed; the 'constant distance from equilibrium' rule does not apply here. All conditions are achieved with an isothermal or slightly positive external temperature profile slope. It is obvious that non-maximum conversion results from these profiles. It is apparent that the optimisation is suggesting that it is better to sacrifice some thermal output in order to avoid the need to provide exergy for pre-heating.

A number of other observations can be made from Figs. 3 and 4. It should be noted that all profiles shown are only approximately optimal. Small variations in temperature profiles near optimum, produce no resolvable variation in the overall change in reaction extent. For higher pressure and massflow combinations, maximum achievable thermal output and maximum net exergy rate are higher, but to achieve it, the temperature difference between inside the reactor and the wall must be higher to support the greater heat transfer. In case of maximum thermal output, wall temperature profiles end up slightly lower and flatter and the 'distance' between average and equilibrium composition curves is increased. In case of maximum net exergy rate, a relatively low gas inlet temperature corresponding to a rather big 'distance' between average and equilibrium composition at the beginning of the bed is sacrificed for a low exergy rate for preheating, as mentioned previously.

3.2.2. Effect of operating parameters and correlation between maximum thermal and exergetic output.

Fig. 5 illustrates the selection of wall temperature profile for maximum thermal power and maximum net exergy output for the case of 20 MPa and 0.9 g s^{-1} operation. Each curve represents a different slope of wall temperature profile, with the average temperature adjusted by variation of the temperature at $z = 0$. The gas inlet temperature was assumed to be 50°C lower than the $z = 0$ wall temperature in each case. In case of thermal output profiles, a clear maximum thermal output level of 993.5 W is evident at an average reactor wall temperature of 475°C , produced with a $z = 0$ temperature of 500°C and a slope of $-0.5^\circ\text{C cm}^{-1}$.

It is apparent that the most important variable is the average wall temperature and that close to maximum power output can be obtained with a range of wall temperature profile slopes.

In case of net exergy rate, maximum output is apparent at 431.82 W , with an average temperature of 494°C produced with $z = 0$ temperature of 475°C and a slope of $0.5^\circ\text{C cm}^{-1}$. This corresponds to 861.58 W effective power, and it is apparent that a sacrifice of $\sim 13\%$ in thermal output results in maximised net exergy rate of the reactor. In the context of an exergoeconomic optimisation, this would be re-interpreted as the need to provide for an $\sim 15\%$ larger reactor in order to achieve the increase in exergy rate output (corresponding to the temperature increase whilst maintaining the same thermal output). This is low

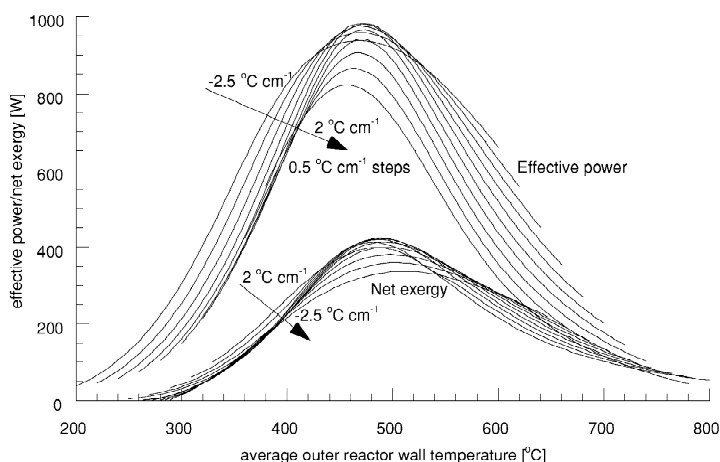


Fig. 5. The effect of varying the outer reactor wall temperature profile on effective power level (top array of curves) and net exergy output (bottom array of curves). Each curve represents runs of linear reactor wall temperature profiles with a constant slope and variable start temperature. Pressure, 20 Pa; massflow, 0.9 g s^{-1} ; reaction extent inlet, 0.98; inlet temperature of the gas was assumed to be 50°C lower than the temperature of the reactor's wall at the start of the bed for all simulation runs.

enough to suggest that such trade-offs are likely to be worth considering.

It is apparent from the array of net exergy rate curves that the most important variable is the average outer reactor wall temperature and that, similar to the 'effective power' array of curves, maximum exergy rate output can be obtained with a range of wall temperature profile slopes. Highest performances can be achieved with slightly higher average temperatures than for maximum thermal power output, as was expected.

The results of Fig. 5 were based on an assumption that the gas inlet temperature was always 50°C less than the wall temperature at $z = 0$. In general the gas inlet temperature is another variable in the optimisation for maximum thermal power and net exergy rate output, however it has been found to be of only minor influence. The sensitivity of reactor geometry was also investigated. In case of maximum net exergy rate, it was found that for a smaller reactor, an isothermal outer reactor profile results in maximum net exergy output whilst a positive slope was needed for maximum net exergy output in case of a bigger reactor diameter. This result tends to favour either very small diameter reactors to get close to the maximum rate curve or adiabatic reactors.

4. CONCLUSIONS

The theoretical study of the laboratory-scale tubular ammonia synthesis reactor has included both optimisation for maximum thermal power and net exergy rate output. Whilst equal 'distance' between average composition curve and chemical equilibrium along the reactor gives maximum recovery of heat, maximum net exergy output is achieved with the internal average composition being close to equilibrium at the end of the bed. Maintaining the best average temperature is important for achieving both maximum thermal power and maximum net exergy. This study shows that a different set of 'optimum' reactor conditions results in optimized or maximum exergy rather than maximum thermal output. Thus, exergy analysis proved to be a useful technique for gathering information about the energy system investigated that would with an energy analysis purely based on first-law analysis not have been accomplished.

Exergy analysis results tend to favour either very small diameter reactors to get close to the

maximum rate curve or adiabatic reactors as used in industry.

This study represents an important step for improved experimental performance of the 1 kW_{chem} laboratory scale ammonia synthesis reactor. The results are important for a complete exergo-economic optimisation of the ammonia-based closed-loop system.

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