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Modelling propane dehydrogenation in a rotating monolith reactor

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Abstract

The catalytic dehydrogenation of propane is equilibrium limited, strongly endothermic and normally carried out at high temperatures. The catalyst deactivates due to the laydown of carbonaceous species on the surface. This is conventionally countered by subjecting the catalyst to periodic regeneration. In commercially available processes, the catalyst time on line for a given cycle is in the order of 10–10,000 min.

In this study, the catalyst has been observed to exhibit very high activity and selectivity in the short period after regeneration. Conceptual and model development of a reactor with structured catalyst to capitalise on this beneficial early activity is presented.

The preferred reactor comprises a cylindrical block of honeycomb monolith that rotates past various feed zones, subjecting the catalyst successively to propane and regenerating gas. The exothermic nature of the regeneration reactions is used at least in part to provide heat to the endothermic dehydrogenation reaction via the regenerative heat transfer facilitated by the movement of the solid monolith. Specifically, it is noted that an oxidisible catalyst provides operating advantage due to the additional exotherms associated with the regeneration stage.

The process modelling shows the design to be feasible in terms of matching the heats of reactions and achieving high conversions, but questions are raised over its practicability from mechanical design and process stability viewpoints.

Keywords: Catalytic dehydrogenation; Monolith reactor; Propane

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1. Introduction

Changes in the demand of propene and isobutene are presenting a need and an opportunity for on-purpose manufacture of these chemicals, as opposed to their traditional sourcing as by-products from steam cracking and catalytic cracking. While various schemes have been proposed for the on-purpose production, the most feasible on a commercial scale at present is catalytic dehydrogenation of the relevant alkane.

The dehydrogenation of propane to propene is typically carried out over a catalyst at approximately 873 K and near atmospheric pressure. The reaction is equilibrium limited and highly endothermic, and therefore heat supply is required through the reaction. Side reactions include cracking to lower hydrocarbons and carbon with some polyaromatics formation. Catalyst regeneration is required due to deactivation caused by the "coke" deposition. Time-scales between regeneration vary considerably for the commercial processes available.

In this paper, we present a reactor concept designed to capitalise on observed very high activity in the very

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early part of the catalyst life after a regeneration by cycling the catalyst rapidly through successive dehydrogenation and regeneration stages. The concept is exemplified using the propane reaction, but the concept is equally applicable to C4 chemistry.

2. Propane dehydrogenation process chemistry

The main reaction, $C_3H_8 \Leftrightarrow C_3H_6 + H_2$, is highly endothermic ($\Delta H = -110\,\mathrm{kJ/mol}$) and is equilibrium limited. At 873 K, a typical operating temperature, conversion is limited to about 50% with very small amounts going through to the propadiene and propyne. This low pass conversion has led to much interest in applying techniques to try and overcome the equilibrium limitation, such as membrane reactor to abstract the hydrogen [1] or oxidative dehydrogenation to sequester the hydrogen as water [2]. As yet, neither of these techniques is sufficiently developed to merit commercialisation, and indeed significant hurdles remain to be overcome for either approach to be commercially feasible.

For the simple catalytic dehydrogenation reaction, the catalysts proposed and used in practice vary considerably, but generally rely on a platinum or chromia active species. These catalysts are not 100% selective, and the basic dehydrogenation reaction is accompanied by various side reactions comprising essentially the cracking of the feed hydrocarbon to lower hydrocarbons and the formation of dehydrogenated carbonaceous species on the catalyst surface. The formation of this “coke” leads to the deactivation of the catalyst, and the catalyst requires regular regeneration to restore its activity. The regeneration consists of burning off the “coke” to re-expose the active sites that have been obscured by the surface deposits.

3. Commercial processes for LPG dehydrogenation

The dehydrogenation of light hydrocarbons has been known and practised for over 50 years [3]. The deactivation and necessity for periodic regeneration is acknowledged and tackled even in this early patent. Actual or near-commercial reactors vary significantly in their approach to managing deactivation and regeneration leading to significantly different reactor concepts.

- Coupling the heat of regeneration and the endotherm for dehydrogenation through cyclic processing (cycle time 15–25 min) of a series of fixed beds where the chromia catalyst is diluted with inert filler to increase the heat capacity [4].
- Using a series of adiabatic beds in series with inter-heating [5,6]. This is based on the UOP continuous catalyst regeneration concept where platinum catalyst moves through the beds over a 3–5 day period. A hydrogen co-feed is used to suppress coking.
- Employing a fired tubular reactor with a co-feed of steam over a Pt/Sn catalyst [7] or hydrogen over a promoted Pt catalyst [8] to suppress coking and deactivation. Typical catalyst on-line times for both are in the order of 6–8 h.
- Using twin fluidised beds, one on dehydrogenation and the other on regeneration with catalyst transfer there between, and regenerative heat transfer [9].

Drawing on these examples, catalyst cycles range approximately from 10 to 10,000 min (three orders of magnitude) and process conditions range over 550–650°C and 0.3–3 bar.

4. Experimental

Details have been previously published relating to the catalyst, experimental methods, experimental data over extended time [10]. In summary, the catalyst used in this study was a modified alumina-supported chromia, prepared by an impregnation route involving drying and calcination. Two isothermal reactor systems were used in this study. Pulsed reaction studies were performed at high space velocity in a dynamic mode using a pulse-flow microreactor system with on-line GC. Continuous flow reaction studies were performed at atmospheric pressure in a microreactor with the gas stream-exit, the reactor sampled by on-line GC. The catalyst was reduced by heating to 873 K in a stream of hydrogen, and then the flow was switched to propane. Regeneration between runs was carried out using air or dilute oxygen, during which the catalyst was also oxidised. The catalyst was then reduced, using hydrogen, prior to feeding propane again.

5. Rotating monolith reactor concept

It was observed experimentally that immediately after regeneration the catalyst has a very high activity (factor 3–5), with near equilibrium conversions being achieved at high space velocities. This initial high activity is rapidly lost, Fig. 1. Selectivities as high as 95% were observed during this initial period. By operating the catalyst only for short periods after regeneration, it appears therefore possible to achieve the twin goals of high conversion and high selectivity.

The driver in the reactor design concept presented herein was to capitalise on this initial high activity and to utilise regenerative heat transfer in an unsteady state reactor. A key question is how to cycle a catalyst at the required frequency — a cycle time in the order of 30–100 s.

Valve switching about fixed catalyst beds will not achieve the necessary speed, and so the approach has to be to move the catalyst across a series of fixed gas feed points. A circulating fluidised bed system similar in concept to that used for FCC, and more recently for the selective oxidation of butane to maleic anhydride [11] was considered, but preference was given to a reactor comprising a mobile-structured catalyst, specifically rotating a honeycomb monolith past zones where propane or air (for regeneration) are fed continuously.

Rotating monoliths have been proposed elsewhere as reactors for concentrating low level components in gas streams such as VOCs [12] and H_2S [13], and for the separation of bulk chemicals such as iso and normal alkanes [14]. The application here is a little more complex, involving use of regenerative heat exchange to thermally link endothermic and exothermic reactions, and potentially increases the thermal efficiency of the process.

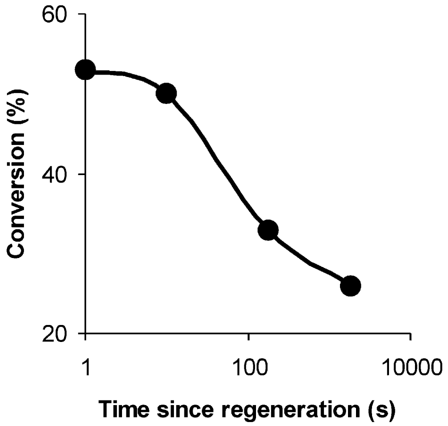

Fig. 1. Catalyst shows high initial activity.

The main drivers in the development of a rotating monolith reactor may thus be summarised as follows:

- structured catalyst bed,
- use of regenerative heat transfer,
- low pressure drop,
- avoidance of high temperature flow switching valves,
- avoidance of flowing granular solids,
- maximised working volume,
- exploitation of observed initial very high catalyst activity and selectivity.

6. Reaction and reactor modelling

The derivation of a kinetic and deactivation model for propane dehydrogenation, including by-product and coking reactions over the same catalyst, has been previously described, but in the context of a more conventional fixed bed reactor [15]. The same reaction model was used in the present study. Overall heat balance calculations, however, showed that the side reactions and coke were not significant contributors to the overall heat balance and so for the purposes of preliminary modelling could be neglected. The modelling reported in the paper considers only the reversible propane dehydrogenation reaction, where the kinetic equation was assumed first order in all components with the rate constant derived from high space velocity, pulsed flow differential experiments and the equilibrium constant calculated from first principles.

A fortran model of the reactor was written to allow evaluation of the potential design. The catalyst temperature and activity cycle were evaluated using a sequential steady-state approach rather than using rigorous partial differential equation solutions. The cycling nature of the reactor means that in fact the overall reactor operates at steady state. That is, while the moving catalyst sees varying temperatures and feeds as it rotates, the condition at a given stationary point is constant. The model included the following features:

- *Dehydrogenation stage reactions*. The assumed kinetics are described above. Calculations showed the reaction was unlikely to be diffusion controlled.
- *Other reactions*. The coke oxidation reaction, and catalyst oxidation and reduction reactions introduced later in the text were assumed to be "fast" (viz. reagent limited). The degree of oxidation/reduction of the chromia was based on experimental data.
- *Heat transfer*. Standard heat transfer correlations are used for gas-monolith heat transfer. Axial, radial and tangential conduction by the monolith are neglected. The modelling in fact showed heat transfer to be very good with gas-monolith temperature differences of 10°C or less.
- *Heat balance*. This included reaction thermochemistry and flowing enthalpies of the gas (axial) and monolith (rotational).
- *Rotational pumping*. As the monolith moves from one zone to the next, it carries with it its inventory of gas fed in the previous segment. This stream mixing effect is included.

7. Preliminary modelling: an air-heated reactor

In early modelling work, a simplistic approach to the process design was maintained, Fig. 2. Regeneration and heating of the monolith and catalyst was by a pre-heated air stream with flow in the "forward" direction. The propane stream was fed in the "reverse" direction with a second pass in the opposite ("forward") direction. The objective of the second pass was to cool the exit stream and to redistribute the heat axially in the monolith. For simplicity, the heat of the regeneration reaction was neglected and only the main propane to propene reaction was considered in the dehydrogenation regions.

The design basis was as follows:

- Monolith volume, 24 m^3; reactor depth, 1 m.
- Monolith cycle time, 30 s:
  - Air, 15 s; reverse propane, 10 s; forward propane, 5 s.
- Heated air feed (forward flow):
  - 7.5 kmol/s, 10 bar(a), 893 K (mean exit temperature, 843.5 K).
- Propane feed (reverse flow):
  - 0.273 kmol/s (GHSV 3000 h^{-1}), 1.1 bar(a), 673 K, 100% propane.
- Propane second pass (forward flow):
  - GHSV 6000 h^{-1}, 1.09 bar(a), 887 K, 77.04% propane.
- Exit stream:
  - 759.5 K, 71.2% propane (17% conversion).

The results are presented in Fig. 3, showing the temperature and composition profiles at the boundaries between adjacent sections. This initial simulation demonstrates that a very large quantity of pre-heated

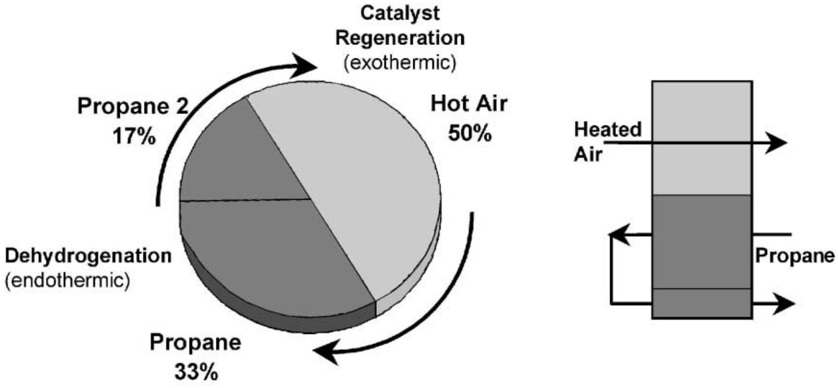

Fig. 2. Preliminary process model.

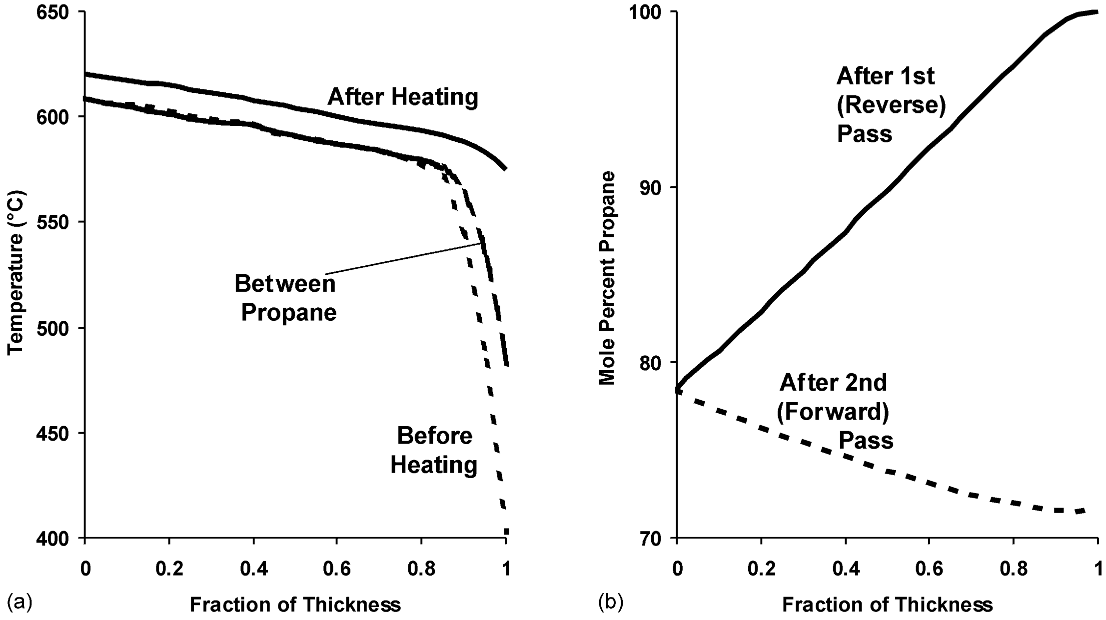

Fig. 3. Results from preliminary simple model.

air is required to satisfy the heat balance. This would in practice require the use of pressurised air to limit the pressure drop and to prevent an unacceptably large proportion of the reactor being in non-productive mode. This simulation also raises questions over the use of the second propane pass. In this design at least, the residence time is too long and this leads in fact to equilibrium reversal of the reaction as the process gas cools. It is, however, effective in redistributing the heat.

In a second study, a similar design was used to consider the effects of the main design variables. For this study, the base case design was as follows:

- Total monolith volume, 6.3 m^3 (3 m diameter × 1 m):
    - ○ 20% air heating (forward flow);
    - ○ 60% propane first pass (reverse flow);
    - ○ 20% propane second pass (forward flow).
- Catalyst loading, 9 wt.%.
- Propane feed rate, 342 kmol/h.
- Propane feed temperature, 673 K.
- Cycle times varied to obtain maximum solid temperature, 923 K.
- Heating air feed temperature, 823 K.
- Reactions: propane $\Leftrightarrow$ propene and carbon oxidation to CO_2.

The runs and results are summarised in Table 1, and the temperature profiles are presented in Fig. 4. The redistribution of catalyst volume has a significant effect on the profiles as compared to those given in Fig. 3. It is clear from these runs that the key in obtaining high conversions is maintaining the whole of the dehydrogenation section at the highest temperature, noting particularly that in Fig. 4c compared to Fig. 4a the catalyst loading is halved and yet a higher conversion is achieved.

Table 1
Design study of an air heated rotating monolith reactor

	Case number		
	1	2	3
Chromia loading (wt.%)	9.0	9.0	4.5
Cycle time (s)	245	129	81.7
Air rate (kmol/s)	0.5	2.0	1.0
Propane conversion (%)	15.8	22.3	18.7

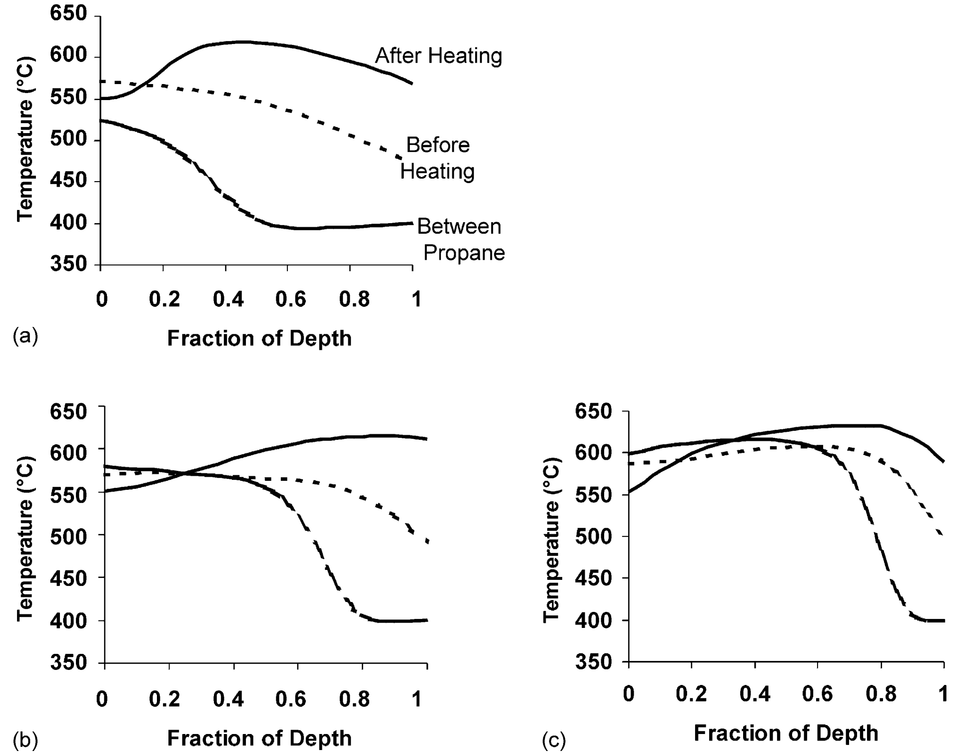

Fig. 4. Effects of process design variables for the hot air-heated reactor.

8. An internally heated rotating monolith reactor

In the case of chromia, it was clear from experimental work that during the carbon burn-off, the chromia itself was oxidised. Laboratory measurements showed that if the regenerated catalyst was not first treated with hydrogen, then the early parts of propane feed were oxidised to CO_2, CO, H_2O and carbon. The catalyst is reducing back to its active state after being oxidised during the regeneration step. In order to maximise selectivity, it was found preferable to carry out a pre-reduction of the catalyst in each cycle using hydrogen. Fortuitously, this leads to the exothermic formation of water, and thus raises the possibility of generating the dehydrogenation heat internally through the oxidation–reduction (both exothermic overall reactions) cycle of the catalyst reducing the need to use a large heated air flow.

Hence, the carbon and chromia are oxidised according to the following representative reactions.

- Oxidation of coke: $C + O_2 \Rightarrow CO_2$.
- Oxidation of chromia: $2CrO + \frac{1}{2}O_2 \Rightarrow Cr_2O_3$.

Catalyst reduction using hydrogen prior to feed of propane leads to the following exothermic reaction.

- Reduction of chromia: $Cr_2O_3 + H_2 \Rightarrow 2CrO + H_2O$.

Heat generation during the oxidation–reduction cycles is proportional to chromia loading and the rotational speed. Hence, design catalyst loading influences the heat balance as well as dehydrogenation activity.

So, in summary for the design of an internally heated rotating monolith reactor, where the heat is generated substantially by the oxidation–reduction cycles of the oxidisible catalyst, the rotational sequence is as follows, see Fig. 5.

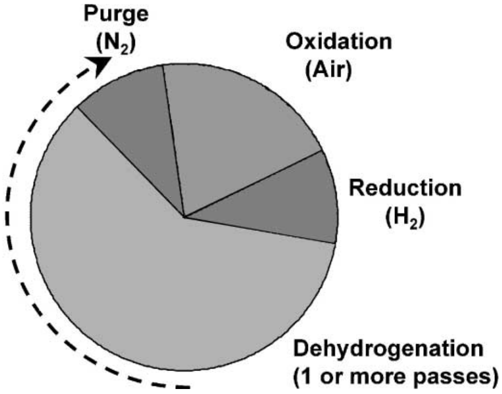

Fig. 5. An internally heated rotating monolith reactor.

- Endothermic:
  - propane feed (dehydrogenation);
  - hydrogen Purge.
- Exothermic:
  - air or O_2/N_2 mix (burns off coke, oxidises chromia);
  - hydrogen feed (reduces chromia).

The rate of dehydrogenation (endotherm) is proportional to the chromia loading and dependent also critically on the catalyst temperature in the dehydrogenation section, while the rate of heat generation is dependent on the chromia loading and the rotational speed.

8.1. Comparison with air-heated operation

Computer simulations of the internally heated design were compared with those for the air-heated design. As above, results from only simple reaction schemes are presented. The presumed reactor layouts are shown in Fig. 6, while the resulting temperature profiles are shown in Fig. 7. It is clear that the internal heating mechanism achieves a much more even temperature profile, and a higher average temperature is possible. The right-hand section of the monolith (as shown) performs the majority of the propane feed preheating. Given the observations already made regarding the need for temperature control to a high level to achieve high conversions, it is evident that the internally heated version is a far better design option. In fact, it is believed that an oxidisible catalyst that allows a substantially internal heating design is essential to the successful design of a rotating monolith reactor to perform an endothermic reaction [16].

8.2. Design studies on the internally heated rotating monolith

A series of simulations were carried out in order to understand the effects of the major design variables. The basic reactor design was as follows. A total monolith of volume 18.85 m^3 was selected. This corresponds to three reactors in parallel, 1 m thick, each of 3 m diameter with a 1 m diameter hub. The monolith channel size of 1.4 mm was selected. The reactors were split into four zones with flows as shown in Fig. 6, but divided into 49% propane (reverse) flow and 17% for each of the other sections. The propane feed rate was set to 1026 kmol/h. This corresponds to 100,000 te/yr of propene at a conversion of 29%. The maximum allowable solid temperature was set at 923 K, and the

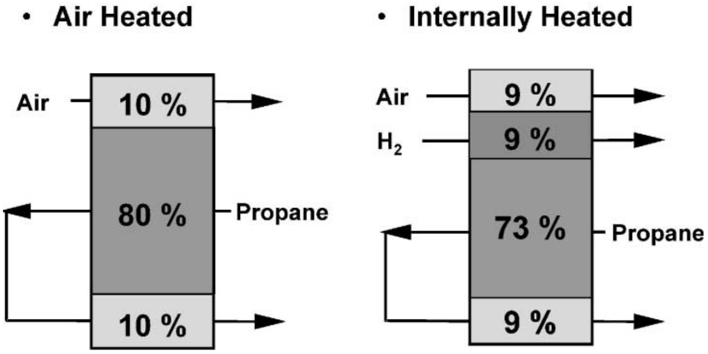

Fig. 6. Comparison of internal and air-heating reactor configurations.

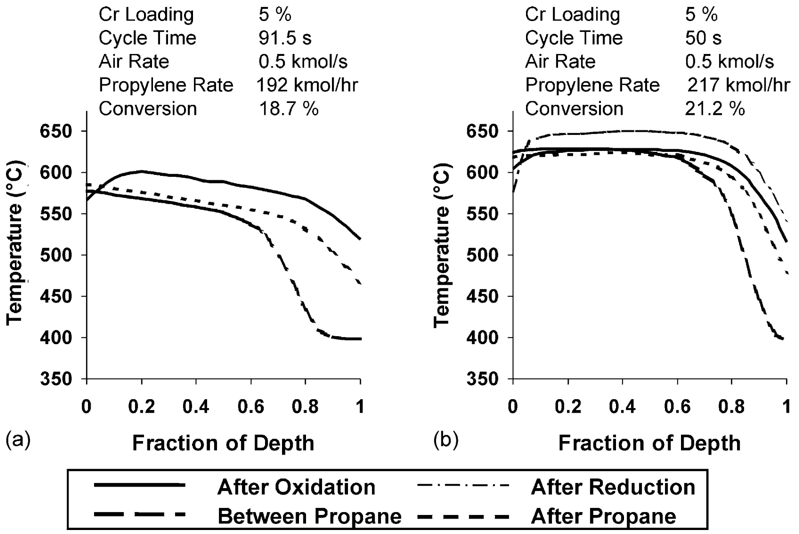

Fig. 7. Comparison of internal and air-heating temperature profiles.

rotational speed varied to achieve this temperature. The reason for this is that the chromia catalyst is known to sinter at significantly above this temperature.

The results from some of these runs are summarised in Table 2, and the temperature profiles shown in Figs. 7b and 8, where Fig. 7b is the base case. In Fig. 7b, the temperature is roughly uniform through the majority of the reactor thickness, which means that the catalyst utilisation is high. The temperature distribution is, however, not optimal.

Table 2
Design study of an internally heated rotating monolith reactor

	Case number		
	1	2	3
Chromia loading (wt.%)	5.0	5.0	5.0
Catalyst activity (–)	1	1	2
Cycle time (s)	50	42	29
Air rate (kmol/s)	0.5	2.0	2.0
Propane conversion (%)	21.2	22.1	35.8

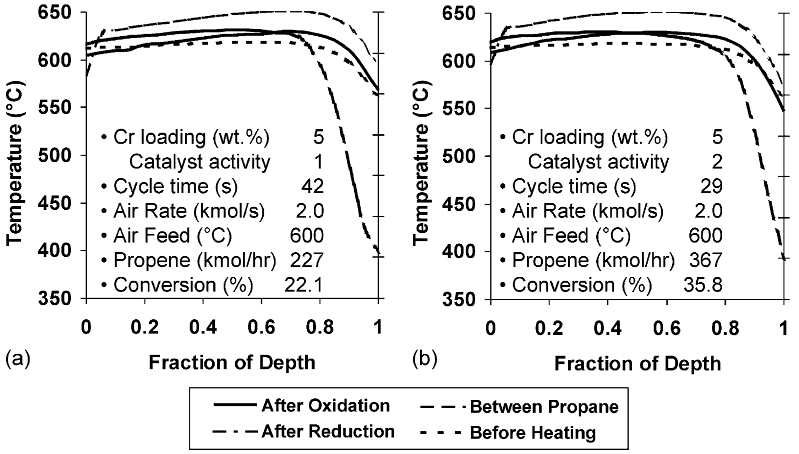

Fig. 8. Effects of process design variables for the internally heated reactor.

Increasing the air rate has a clear effect on the temperature profile, Fig. 8a, effectively pushing the heat towards the back of the reactor. This gives a slightly increasing temperature through the reactor, which is known to be beneficial to operation [17]. Accordingly, an increase in conversion is witnessed. The reality is, however, that in this case, the performance of the reactor is no longer thermally limited, but rather limited by the assumed activity of the catalyst. Arbitrarily increasing the catalyst activity by a factor of 2, Fig. 8b, with an increase in rotational speed to maintain the heat balance, the conversion can be increased to very high levels.

Clearly, from this with a matched design (surface area, catalyst loading, segment volumes) and operational practice (rotational speed, propane and air rates), it is possible to achieve high propane conversion rates.

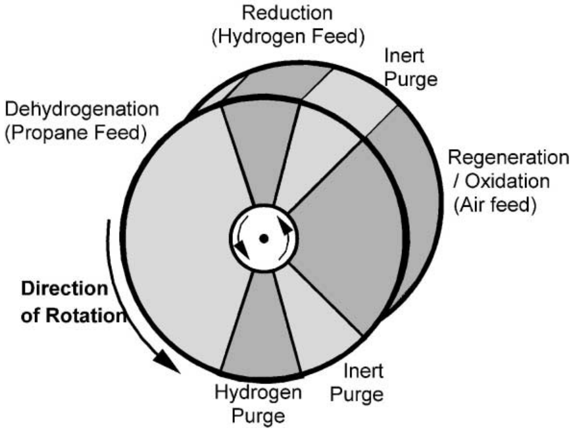

Fig. 9. Layout of the rotating monolith reactor.

9. Reactor design considerations

The main challenges in the realisation of an operable rotating monolith are in fact related to process safety and mechanical design.

In terms of process safety and operability, the dynamic seals to the rotating monolith are probably not 100% effective. An inert purge is, therefore, required to isolate oxygen-containing stream from combustible feeds, and hence on both sides of the regeneration zone. The overall layout of the proposed final rotating monolith design is shown in Fig. 9 and an outline flowsheet given in Fig. 10. It is a moot point as to whether the various gas/feed interchangers would be better replaced with extra rotational monolith volume (maybe not catalytically active) to capitalise on the higher thermal efficiency of regenerative, rather than recuperative heat exchange.

The seals must be robust and not lead to erosion of the monolith. Monolith durability is an issue, and

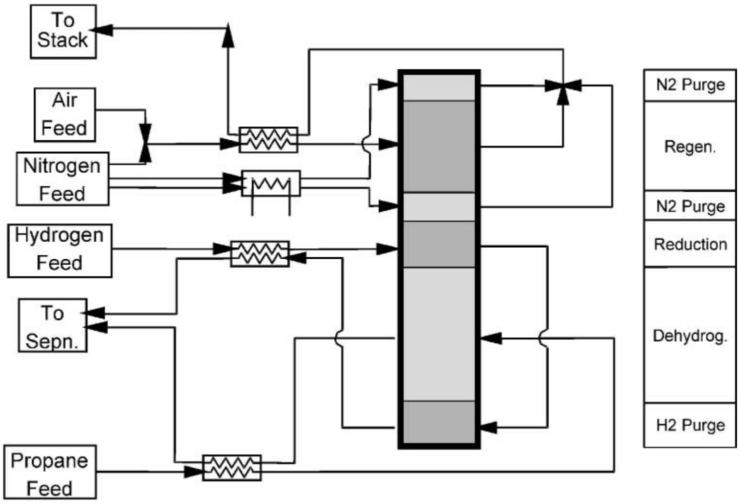

Fig. 10. Schematic flowsheet for a propane dehyrogenation "wheel" reactor.

for reasons above and beyond erosion of the ends over each cycle. At a frequency of one or more per minute, the monolith is cycled through wide temperature fluctuations as it rotates through the different thermal zones and this in turn leads to large temperature gradients across a given monolith block. It is believed that for a process such as propane dehydrogenation where the temperature swings are quite pronounced, the temperature gradients generated may in fact exceed the tolerances on some conventional monolith ceramics, and specifically alumina is probably not feasible [18]. In addition to these mechanical concerns, recent work on the multiplicity of reactors with thermally coupled endothermic and exothermic reactions [19] should be equally considered. Whether this would in fact be mitigated in this particular reactor by the dominating influence on the heat balance of the catalyst oxidation–reduction exotherms is a moot point, and one that has not yet been considered.

10. Conclusion

Experimental data show potential activity benefit of fast catalyst cycling, with high activity in early period after regeneration. Modelling work has shown process feasibility of a rotating monolith reactor, with the rapid catalyst cycling (order of 1 min or less) and exploiting regenerative heat transfer between the exothermic regeneration and endothermic dehydrogenation sections.

The heat input into the reactor is ostensibly via coke combustion and heated air. The best performance is, however, achieved if the monolith is self-heating during this phase. This can be achieved though the use of an oxidisible catalyst, such as an oxide catalyst or specifically in this instance, chromia. The catalyst is oxidised under the oxygen along with the combustion of the coke, and then reduced under hydrogen (exothermic courtesy of the associated hydrogen combustion). Under rapid cycling conditions, this oxidation–reduction cycles of the catalyst becomes the dominant heat generation term and helps assure a reasonably uniform temperature axially through the monolith.

Pseudo-steady-state modelling of the reactor has thus shown the feasibility of the reactor and of its application to the propane dehydrogenation reaction. A major uncertainty remains, however, regarding the potential robustness and operability of the reactor relating to both the mechanical integrity and the process stability and controllability.

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