HEX-REACTOR APPLICATIONS IN THE NETHERLANDS

A non-confidential summary

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Preface

This work is a non-confidential summary of the project 'HEX-reactor applications in the Netherlands' which was carried out in the period 2000-2002. Funding for this project was provided partly (for 50%) by the Novem. The project was carried out by ECN in co-operation with Chemserve and Process Design Center (PDC). ECN project number: 76424. Novem project number: 304307/0030.

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Abstract

The HEX reactor (heat exchanger reactor), which combines a chemical reactor and heat exchanger in one compact unit, has not found significant application in industry, despite many potential advantages including energy savings. In the current project the objectives were:

- To identify two promising applications for demonstration projects in the short term.
- To make a broad inventory of applications covering all types of processes from which two will be selected for longer-term development.

The search for a demonstration project was focussed on processes with exothermic liquid-phase reactions without heterogeneous catalysis. Energy savings for this application are probably 2-8 PJ/y (in the Netherlands). Detailed evaluations were made for two promising processes, which were selected: a polymerisation and an oxidation process. Application of HEX reactors to the selected polymerisation process was judged to be not suitable for a short-term demonstration project, and the potential savings were estimated to be less than about 0.25 PJ/y (in NL). For the selected oxidation process, simulations of one plant showed potential energy savings of about 0.6 PJ/y as well as other advantages, such as improved product yield. In view of the high repetition potential for other oxidation processes, this could be an interesting demonstration project.

In the broad inventory, twenty-two HEX-reactor applications were identified, with total energy savings, which could amount to 20 PJ/y (in NL). Detailed evaluations were done for two large-scale processes with heterogeneously catalysed gas-phase reactions. For the first process, energy savings are estimated to amount to about 2 PJ/y (in NL), but the commercial potential is judged to be small. For the second process, energy savings are up to 4.2 PJ/y (in NL), possibly together with cost savings, and this could be of interest for long-term development.

Keywords

Heat exchanger reactor, HEX reactor

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SUMMARY

Recently there has been a growing interest in the HEX reactor (heat exchanger reactor), which combines the traditional operations of chemical reactor and heat exchanger in one compact unit. Most recent developments have concentrated on the application of commercially-available compact heat exchangers as chemical reactors. However, despite many potential advantages including energy savings, HEX reactors have still not found significant application in industry. In the current project the objectives were:

- To identify two promising applications for demonstration projects in the short term.
- To make a broad inventory of applications covering all types of processes from which two will be selected for longer-term development.

The search for a demonstration project was focussed on processes with exothermic liquid-phase reactions without heterogeneous catalysis. Starting with a list of about 100 companies/processes, suitable criteria were used to produce a short list. A more detailed ranking was then done, based on contacts/visits with the companies concerned. Energy savings achievable by implementation of non-catalytic HEX reactors in the Netherlands are probably in the range 2-8 PJ/y. More detailed evaluations were made for two processes: a polymerisation and an oxidation process.

For the selected polymerisation process, a HEX reactor has some advantages, especially by enabling a switch from batch to continuous operation, but it may be essential to leave the current operating window. Furthermore, the polymerisation mechanism is complex, and product quality is sensitive to reaction conditions. Therefore this application is not very suitable for a short-term demonstration project. The energy savings were quantified for a typical plant, and on this basis the potential savings for the Netherlands are estimated to be less than about 0.25 PJ/y.

For the selected oxidation process, simulation showed that HEX reactors lead to a slightly improved selectivity, and to a beneficial change in the product distribution. The potential energy savings are about 0.6 PJ/y for this plant. These savings, together with the high repetition potential for other oxidation processes, could make this an interesting demonstration project.

In the broad inventory, more than 50 important chemical processes have been evaluated on the benefits expected from HEX reactor application, with a focus on energy savings. In total 22 applications were identified. The total theoretical room for improvement in these processes is about 200 PJ/y for the Netherlands. Based on the assumption that the application of HEX reactors in these processes would lead to an energy saving of 10 % on average, total savings amount to 20 PJ/y. More detailed evaluations were done for two processes. Both are large-scale processes with heterogeneously catalysed gas-phase reactions.

For the first process, HEX reactors are more compact than the conventional reactor and offer a better temperature control. They are especially well suited for thermally coupling the endothermic and exothermic reactions in the process. Energy savings in the order of 2 PJ/y can be expected in the Netherlands. However, HEX reactors do not bring major step changes compared with state-of-the-art reactor designs. Also, it is not expected that their application will reduce the capital investment. Therefore, the commercial potential for large-scale, industrial processes is judged to be small. It is expected that HEX reactors in this area will first be applied for small-scale applications.

For the second process, a HEX reactor can achieve higher per-pass conversions by operating along the optimum temperature profile. The advantage is a higher total production rate or a reduced size of the gaseous recycle loop. First calculations show that energy savings up to 4.2 PJ/y can be achieved in the Netherlands, possibly together with cost savings. This application could be of interest for long-term development.

1. INTRODUCTION

1.1 Background and problem definition

It is now generally recognised that in order to meet the demands of society in the coming decades, industry must begin to use processes, which are more sustainable or eco-efficient. In particular, the trend of improving energy efficiency, which has been established in the last decades, must be maintained. Up till now, energy savings and environmental goals have been achieved mainly by using existing technologies or by making incremental improvements to such technologies. However in order to maintain the trend of energy-efficiency improvement in the future, it will be necessary to develop and apply novel breakthrough technologies which can transform industrial processes in a more fundamental and radical fashion.

In recent years there has been an increasing interest in *process intensification*, which aims to replace the traditional unit operations with novel, usually very compact designs, often by combining two or more traditional operations in one hybrid unit. Process intensification itself covers a rather wide range of possibilities. Here we focus on applications in the chemicals sector, which is the largest industrial energy user. Furthermore, we focus on a new technology, which directly affects the heart of the process, namely, the chemical reactor, since this has potentially the greatest impact in the longer term. This technology is the HEX reactor (heat exchanger reactor) which intimately combines the traditional operations of chemical reactor and heat exchanger in one compact unit.

In 1998 BHR conducted a survey on behalf of NOVEM into the benefits of HEX reactors for the Dutch chemical industry [1]. The conclusion of the BHR report, that HEX reactors can bring great benefits, including substantial energy savings, is (in our opinion) correct. However, the evidence presented by BHR was not very substantial. In particular the report has the following limitations:

- It is based on limited information from a few large companies. But many of the relevant processes may be located with smaller companies.
- Examples are given only for a few representative processes; no overall survey of processes is attempted. Accordingly, many relevant processes are not addressed.
- Global data for energy use of processes are given for the UK or EU; no specific data are given for the Dutch situation.

Although the BHR report and other studies have highlighted the potential benefits of HEX reactors, such reactors have still not found significant application in industry. The main barrier to implementation is that there are few (if any) practical examples to demonstrate the operations and advantages of this technology. The development of a strategy for industrial implementation is hampered by the lack of information about the extent, nature, and location of potential applications in the Netherlands. This makes it difficult to

- quantify the incentives,
- identify the most feasible applications,
- make contact with potential end-users, especially in the smaller companies.

1.2 Project objectives

In the current project (considered to be Phase 1 of a larger project) the objectives are:

- To identify at least two promising applications for demonstration projects in the short term. This search is focussed primarily on processes which are based on fast exothermic liquid-phase reactions and which currently use stirred tank reactors. This is because prior research on this type of HEX-reactor application is relatively advanced, and many of these processes are small-scale.
- To make a broad inventory of applications covering all types of processes from which two will be selected for longer-term development.

Not included in the current project are Phases 2 (proof of principle) and 3 (demonstration). The ultimate objective is to realise substantial energy and environmental savings by applying HEX reactors in the Dutch chemical industry.

1.3 Project reporting

The results have been reported in a series of confidential reports:

- Volume 1: general introduction and overview of HEX reactors.
- Volume 2: the search for a demonstration project.
- Volumes 3 and 4: detailed evaluations of the two most promising candidates for demonstration projects (short-term application).
- Volume 5: the broad inventory.
- Volume 6 and 7: detailed evaluations of the two most promising candidates from the broad inventory (more long-term application).

The current report is a non-confidential summary of the above reports.

2. AN OVERVIEW OF HEX REACTORS

The following overview is based on a survey of the open literature.

The HEX reactor is a piece of equipment, which combines the functions of a chemical reactor and a heat exchanger in an intimate fashion. Most recent developments have concentrated on the application of commercially-available compact heat exchangers (CHEs) as chemical reactors. The HEX-reactor technology potentially offers many advantages such as improved selectivity and yield, savings in costs and energy, less environmental impact, and better safety.

Energy savings may arise by several mechanisms, not only directly (the reactor itself may be more energy-efficient) but also indirectly (e.g. improvements in yield or selectivity lead to energy savings downstream). However the energy savings attainable in practice may be limited either by intrinsic process factors (thermodynamics/kinetics) or by external constraints (e.g. the heat integration at the site).

Non-catalytic HEX reactors have advantages for carrying out fast exothermic liquid-phase reactions, as an alternative to stirred tank reactors, which are mainly applied in small-scale batch processes. The technology has been researched for liquid-phase systems, but more remains to be done for gas-liquid systems.

Catalytic HEX reactors have several advantages for gas-phase reactions. The clearest incentive seems to exist for combined HEX reactors which thermally couple catalytic combustion with a strongly endothermic reaction, as an alternative to conventional fired furnaces. However application to large-scale processes is a long-term objective. Catalyst coating techniques, catalyst lifetime, and HEX-reactor design are the main R&D issues.

Although HEX reactors are based on proven technology (CHEs) there are many hurdles to be overcome before they are generally accepted in the chemical industry. Potential hurdles include issues such as fouling/plugging, corrosion, catalyst design and replacement, fabrication of units for high process temperatures and large-scale applications, and capital investment costs.

Microreactors (which have a smaller channel size than HEX reactors) have recently attracted much attention and may have an impact on the chemical industry in the long term, but in the short term HEX reactors have a greater chance of acceptance.

3. THE SEARCH FOR A DEMONSTRATION PROJECT

3.1 General procedure

The search for suitable short-term demonstration projects for HEX reactors in the Dutch chemical industry was carried out as follows. Processes using heterogeneous catalysis were excluded because such applications are expected to require longer development times. The search was focussed primarily on processes which are based on fast exothermic liquid-phase reactions and which currently use stirred tank reactors. First, a long list of about 100 companies/processes was compiled. Suitable ranking/selection criteria were developed, with which the long list was screened to produce a short list of about 10 processes. For the short list a more detailed ranking was done, based on contacts with and visits to the companies concerned. Finally the two most promising applications were selected for more detailed evaluations, which are reported in sections 4 and 5.

3.2 The long list

A long list of companies/processes was generated as follows. The Chamber of Commerce data with an SBI code starting with DG24 or DH25 concern approximately 1500 companies, which is in principle too much and also covers small retailers, which are not of interest in this study. There are 80 VNCI members, who cover the bigger companies with a certain interest and economic impact. (One company can have more than 1 site). There are 110 'BMP-inrichtingen'[1], which are significant sites in the Netherlands from an environmental perspective. There are 85 chemical companies who signed the MJA1 (Meerjarenafspraken 1) which gives an idea of the number of companies with significant energy usage. It was concluded that the VNCI members combined with the MJA1 list should cover the population of interest in the Netherlands. This combined list was used as starting point for further evaluations.

3.3 Ranking criteria

The following criteria were adopted as a means of ranking the processes in the long list:

- Energy savings (preferably through better yield, selectivity, or product quality).
- Repetition potential (how many more similar units? 'similar' with broad interpretation).
- Expected interest of end-user (enthusiastic partner, good prospect).
- Experimental constraints:
  - Knock-out constraints:
    - no solids/slurries,
    - no high-viscosity liquids,
    - no heterogeneous catalysis,
    - no carcinogenic materials.
  - Preferences:
    - low risk materials (toxicity, explosivity, corrosivity),
    - operating conditions as close as possible to 20°C, 1 bar,
    - preferably single liquid phase,
    - chemical analysis techniques available.
- Patentability.
- Image: preferably a 'green process'.

[1] BMP = BedrijfsMilieuPlan

Some further criteria, although in principle important, could not be realistically taken into account in the initial ranking stages because sufficient information was not likely to be available. Such factors were however considered during the visits to companies:
- costs,
- operability/control/safety/environment,
- facilities/infrastructure at end-user site.

3.4 The short list

By applying the above-mentioned criteria to the long list, a short list of processes was generated. Potential demo projects were identified in 4 categories:
- Polymerisations (6 companies of which 2 were selected for contacts/visits).
- Oxidations (3 companies, all selected).
- Condensation reactions (2 companies, both selected).
- Halogenations (1 company, selected).

Three other companies were felt to be of interest because they have many small-scale processes but insufficient information was initially available to make a good assessment. Furthermore, as a result of an article about our project in the NCI magazine, enquiries were received from 2 other companies. Accordingly, contacts/visits were made to these companies as well.

3.5 Contacts and visits

Polymerisations

A number of incentives were identified for application of HEX reactors to the liquid-phase polymerisation processes of one of the two companies. Currently batch reactors are used. HEX reactors would allow continuous operation, which implies higher productivity, with cost and energy savings. Other advantages include better safety, smaller plot size, less fouling problems, and reduction of waste streams.

Oxidations

The contacts/visits confirmed the liquid-phase oxidation process at one of the three companies as a possible demo project. The main interest from the company was in selectivity improvement and possibly safety.

Condensation reactions and halogenations

Contacts with the three companies established that they had insufficient interest in new technology to consider demonstration projects for these processes.

Miscellaneous

Another company identified two processes of potential interest. Potential benefits were seen in terms of smaller equipment, better safety, lower investment, and higher yields. However the company judged that the effort required for implementation was too great, and they were very reluctant to pursue this any further.

Another company was mainly interested in HEX reactors as a means to switch to (semi) continuous production. Benefits were envisaged in terms of waste reduction (cleaning solvents). There was insufficient knowledge about process fundamentals to judge whether other benefits might apply. Implementation would require extensive lab-scale experiments with hazardous material.

Another visit established a picture of a (typical?) pharmaceutical company, which is driven by *product* development and where *process* improvement as such has a low priority. The multipurpose stirred tank is firmly established in the company culture. The HEX reactor would probably first have to be established as a chemist's lab-scale development tool. The company, although interested in the technology, sees no possibilities in the short term.

3.6 Final selection

Based on the above visits/contacts, the best prospects for a demo project were judged to be (in order of choice):
- oxidation,
- polymerisation,
- condensation reactions (despite lack of interest of companies).

Detailed evaluations of the first two choices were done and are which are reported in sections 4 and 5.

3.7 Size of potential market

The search for a demonstration project was focussed primarily on processes which are based on fast exothermic liquid-phase reactions and which are currently done in stirred tank reactors. The literature on HEX reactors, especially the publications of BHR, had led us to expect that we would easily identify many promising candidates from which to make a final selection. However in practice relatively few processes with this ideal 'profile' could be found. This may be because the Dutch chemical industry has relatively few of these processes compared to the UK industry, which is the basis for BHR's experience. Although the Dutch and UK chemical industries are of about the same total size, the distribution among types of process is different.

This relative lack of candidates has two consequences. First, it reduces the chance of identifying a candidate, which fulfils all requirements, and makes it more likely that the final choice will be some kind of compromise. Secondly, it implies that the potential market for the technology to be demonstrated is smaller than expected. Previously, based on an extrapolation of BHR's figures, we had predicted energy savings of about 8 PJ/y by implementation of non-catalytic HEX reactors in the Dutch chemical industry. Based on the work described in this report, it now seems that this figure may be on the high side. Although insufficient data are available for real quantitative estimates, it now seems more likely that the figure is somewhere in the range 2-8 PJ/y.

3.8 Incentives and hurdles for implementation

Some incentives/hurdles were mentioned already in section 2. Here we summarise those items, which emerged specifically from the discussions with potential end-users:

Incentives:
The incentives most often mentioned by the potential end-users were the switch from batch to continuous operation, reduction of waste streams, and safety. Improved yields and decreased size were also important. Improved selectivity was less often mentioned, although this may have been due to uncertainty about the potential benefits of greater selectivity. Energy saving *as such* is not a high priority, and rarely contributes significantly to cost saving.

Hurdles:
Several companies expressed zero interest in this new technology and this seemed to reflect the notorious conservatism of the industry, a 'non-invented here' syndrome, and/or fears of know-how contamination.

Another reason for a weak interest in some cases is that many chemical producers do not consider equipment development as their core business. As long as HEX reactors are not proven technology, which can be bought 'off the shelf' from equipment manufacturers, the producers will have to invest in equipment research and be willing to carry the risk.

In other cases, even when some potential advantages were perceived, it was evident that a switch to HEX reactors would require an enormous *cultural* change within companies which had for many years based all their developments and operations on familiar, flexible, multipurpose batch tank reactors. Such companies were often strongly *product-orientated* with little room for process development. Furthermore, in many cases the fundamental knowledge about reaction kinetics etc. was not available, which means that extensive effort is required even to investigate the feasibility of the new technology. In these circumstances the adherence to traditional methods is a self-perpetuating situation.

Other practical hurdles in finding a suitable process for a demonstration project of HEX reactors are the stringent demands placed on candidate processes. As most chemical processes are (heterogeneously) catalysed nowadays, the constraint of a non-catalytic process ruled out most of the (interesting) candidates.

Finally, one should realise that the implementation of a HEX reactor cannot be done stand-alone. It touches the heart of the process and therefore often requires substantial changes in other parts of the process as well. Consequently, plant owners will only consider the application of a HEX reactor when there is a major (financial) benefit to be gained or in the framework of a major revamp project or for an entirely new plant.

4. EVALUATION OF A POLYMERISATION PROCESS

Certain types of liquid-phase polymerisation process were identified as potential HEX-reactor applications. A number of chemical companies in the Netherlands, and many more world-wide, use these types of process.

Based on a survey of the open literature, it appears that the application of HEX reactors to these types of process might indeed create some interesting options. Current commercial processes are mainly (semi-)batch, and it could be advantageous (for energy savings, among other things) to switch to a continuous process. A HEX reactor has advantages for this type of reaction (plug flow with good radial mixing and heat transfer) but on the other hand it is difficult for a single-pass HEX reactor to provide the long residence time (several hours) which is characteristic of the current processes. Nevertheless current commercial experience suggests that loop configurations may be of interest for some processes, despite the potential disadvantage of a broader residence-time distribution. Single-pass configurations combined with a change of operating window (e.g. higher temperatures), or various hybrid configurations, might also create new opportunities (higher reaction rates, better product quality, new products).

However the complexity and lack of fundamental understanding about the reaction mechanism is accompanied by a great sensitivity of the product quality to the reaction conditions. In order to get the maximum benefit from HEX reactors, it may indeed be essential to leave the current operating window. It might actually be a challenge to avoid a negative effect on product quality compared to the current highly-optimised batch processes. Therefore, it was concluded that this process was not after all suitable for a short-term demonstration project. Rather, any development should be a long-term enterprise, done in close co-operation with polymerisation specialists, both industrial and academic.

In addition, the most important energy savings were quantified for a typical polymerisation plant, using general information obtained from one of the companies concerned, and assuming a switch from batch to continuous operation. On this basis the total potential saving for the Netherlands was estimated to be less than about 0.25 PJ/y.

5. EVALUATION OF AN OXIDATION PROCESS

This large-scale process produces several products by liquid-phase oxidation with air; the reaction is highly exothermic and currently takes place in tank reactors. Several other companies in the Netherlands, and many more world-wide, have similar processes. The application was identified as a good prospect for energy savings and possibly higher selectivity.

Simulations were performed with Aspen Plus, starting with an appropriate base-case model of the reactor section provided by the company. In the simulations, the existing tank reactors were replaced by HEX reactors, modelled as isothermal plug-flow reactors. The simulations investigated the effects of operating temperature and pressure, the use of oxygen in place of air, and the use of multiple air/oxygen feeds in the reactors. All simulations were done with the same production rate and liquid-phase conversion as the base case.

The simulations showed that the application of HEX reactors leads to a slightly improved selectivity, and to a beneficial change in the product distribution. However in order to reduce the size of the HEX reactors to reasonable proportions, the reactors should work at higher pressure and use oxygen instead of air; these conditions also lead to a reduction in the recycle to the reactor. The use of multiple oxygen feeds also helps to reduce the reactor size. The reactor size is determined by the reaction kinetics and is not limited by the heat-transfer requirement.

A preliminary assessment of the energy savings identified a potential saving of 0.6 PJ/y for this plant. The saving is mainly due to the heat recovery in the HEX reactor, but also to the smaller recycle to the reactor, which reduces the pre-heating duty.

Further work will be required to find the optimum working point for the reactor. Not considered in the present study are the economic feasibility, several process constraints and effects such as that of increased or decreased by-products formation on the performance of the work-up section. The hydrodynamics of operating a HEX reactor with a multiphase (G/L) system, and the possible benefits of multiple reactor feeds, should be further evaluated.

The application of a HEX reactor in the process seems an interesting demonstration project in view of the high potential energy savings and the high repetition potential for other liquid-phase oxidation processes.

6. BROAD INVENTORY

6.1 General procedure

The broad inventory is not restricted to those applications, which can be studied or implemented on short term, but also includes applications, which will require long-term development work. In particular, processes using heterogeneous catalysis are included. The broad inventory was carried out as follows. First, a long list of more than 50 important processes was compiled. These processes were evaluated on expected benefits from HEX reactor application. Suitable ranking/selection criteria were developed, with which the long list was screened to produce a short list of processes. For the short list a more detailed ranking was done, partly based on contacts with and visits to the companies concerned. Finally the two most promising applications were selected for more detailed evaluations, which are reported in sections 7 and 8.

6.2 The long list

The lists composed by Chemserve with the largest base-chemicals, organics, inorganics and refinery processes (based on world production capacity) was taken as starting point. A first screening was made to eliminate those processes where:

- There is no producer in the Netherlands.
- The reaction cannot be performed in a HEX reactor (e.g. solids).

After the first screening more than 50 of the most important processes were left for evaluation on HEX reactor application. The process data that were used are primarily based on open literature information and focus on the most important route and most representative process layout. In some cases a specific process or production route is evaluated, because this is the route used by the Dutch manufacturer(s).

A data base was made in which for each process the route and reactions taking place are briefly described. Further, the manufacturers in the Netherlands, their production capacity and the world production (capacity) are indicated. Main process data are given, which are typical for the process route described. The energy data obtained for the whole process are subject to uncertainty, because they are based on literature data. It is not always clear, what is considered inside battery limits (ISBL), what are the feedstocks and whether by-products, which are used as fuel, are included or not. Based on data for fuel, steam and electricity consumption, the total energy consumption is calculated in Primary Fuel Equivalents (PFE).

6.3 Ranking criteria

An assessment is made on several parameters regarding the potential benefits of HEX reactor application in the process. For each parameter a score was given according to the scheme:

++ = Strong improvement expected/strong argument for HEX reactor application.
+ = Improvement expected/argument for HEX reactor application.
0 = No benefit or influence expected/no reason to apply HEX reactors.

The assessment focused on the following parameters:

1. *Exo-/endothermicity*: The more exo- or endothermic the reaction, the more potential there is for HEX reactors. The heat of reaction in kJ/mol is used as a measure. Processes with an absolute heat of reaction larger than 200 kJ/mol are most interesting for HEX application and score '++'. Endothermic processes, which require very high reaction temperatures (500°C or higher) also score '++'. Between 100 and 200 kJ/mol absolute, the score is '+' and between 50 and 100 kJ/mol absolute '0/+'. When the absolute heat of reaction is smaller than 50 kJ/mol the reaction is less interesting for HEX reactors and scores '0'. The (maximum) adiabatic temperature change would be a better measure for determining HEX reactor potential. However, in order to calculate the maximum adiabatic temperature change, the heat capacity of the reaction mixture and dilution ratio must be known. A complication is that the maximum adiabatic temperature change can be different from one plant to the other.
2. *Energy*: A qualitative assessment is made of the potential energy savings that could be achieved with a HEX reactor. It is tried to make a distinction between the energy savings expected in the reactor itself and energy savings in the rest of the process. The assessment is often not straightforward, because in most cases a more detailed study of the reaction and process is required. For example, in order to achieve energy savings, changes in the design of the process or utility system may be required. Heat integration options may change. Changes in reaction selectivity or by-product yield may become so important that step-changes are possible, e.g. a separation task becomes superfluous. The general rule, which was used in the present study, is that energy savings in the reactor are identified, when the reactor efficiency will significantly improve, higher reactant concentrations can be used or the reactor can operate with a higher throughput. For the process, energy savings are mainly expected when selectivity or yield can be improved (smaller separation units/process) or when the conversion per pass can be increased (smaller recycles).
3. *Product yield*: Based on qualitative data on reactions and current reactor performance, an assessment is made of the potential improvement of conversion, selectivity and yield. With conversion, the conversion per pass (through the reactor) is meant and not the overall conversion. Conversion, selectivity and yield can improve, because of the better temperature control that can be achieved with a HEX reactor, but can for instance also be due to the plug flow characteristics of the HEX reactor.
4. *Technical feasibility*: For the assessment of the technical feasibility of a HEX reactor it was taken into account that long term development is allowed. Important issues, which seem difficult to solve at present may be overcome in the future. Therefore, detailed aspects, such as type, size and construction of the HEX reactor and how to apply the catalyst (coating/filling), are not considered. However, in case important hurdles or problems are foreseen, the score is not '+'. A distinction is made between hurdles (score '0/+') which are for instance fouling, short catalyst lifetime or frequent catalyst regeneration, high temperature and highly corrosive conditions, and major problems like plugging with solid product.
5. *Safety/explosion hazard*: In principal, safety is always improved when combustible components are present in the reactor and the reactor size can be reduced. The evaluation focuses on those situations where significant improvement of the safety or reduction of the explosion hazard can be achieved with HEX reactors. Major improvements are expected for very exothermal reactions, especially oxidation reactions, high temperature reactions or when dangerous chemicals are involved.
6. *Reactor size*: One important characteristic of HEX reactors is their compactness. Therefore, reactor size reduction will be a benefit in all cases. Very large reduction in reactor size is possible when the residence time can be reduced, when a HEX reactor replaces very voluminous reactors or reactor sections such as a fluidised bed, a furnace or a cascade of reactors.

7. *Product quality*: In most processes the product quality is determined by the separation rather than the reactor performance. However, the concentration of certain impurities in the final product may be reduced by improvement of the reactor performance. Also the product distribution can be different for a HEX reactor.
8. *Batch to continuous*: HEX reactors may allow to change from batch to continuous operation. This has many advantages, such as energy savings in the utility system and heat integration options, constant product quality, and lower variable cost. Most processes that were evaluated are however already operated continuously.
9. *Throughput/production time*: In many cases the improved temperature control and higher heat fluxes of HEX reactors allow working at a higher reaction rate, which leads to an increase of the throughput or a decrease in production time.
10. *Capital/manufacturing cost*: Assessment of the influence of HEX reactors on the capital cost was not made. Capital cost estimates of a HEX reactor, specifically designed and optimised for application in the process considered, is a complex task. HEX-reactors are not yet state-of-the-art and long-term developments may be required before they can be implemented. Capital cost changes may also occur in other parts of the process, because of improved reactor performance. More detailed evaluation is required in order to assess (capital) cost benefits.

From the +/- scores for each parameter an overall score was calculated for each process, with extra weight being given to energy savings.

6.4 The short list

It was found that the processes, which are most interesting for HEX reactor application, are often characterised by:
- high heat of reaction,
- large world capacity,
- high reaction temperature.

This is not surprising, because the potential for energy savings in these types of processes are high. One of the major advantages of HEX reactors is the ability to control strong endo- or exothermic processes.

The types of processes, which turn out to be especially interesting for HEX reactor application with the view to save energy, are:
- oxidation/oxidative dehydrogenation,
- (hydro)cracking,
- dehydrogenation,
- condensation,
- ammoxidation,
- polymerisation,
- reforming.

A total of 22 processes were identified for HEX application. For these processes, the total energy consumption in the Netherlands is about 200 PJ/y.

For each process, the minimum theoretical exergy use (thermodynamic limit), corresponding to an idealised process without exergy losses, was also calculated. The difference between the actual energy consumption and the theoretical minimum indicates the maximum theoretical room for improvement, based on 100% reaction selectivity and no exergy losses. The total theoretical room for improvement amounts to approximately 200 PJ/y for the identified processes in the Netherlands. Of course, it will not be feasible to achieve these maximum savings. However, when it would be possible to save on average 10% with HEX reactors in these processes, the annual savings for the Netherlands are considerable, amounting to 20 PJ/a.

6.5 Final selection

Based on end-user contacts and internal discussions and evaluations, two applications were selected for further evaluations. Both applications are large-scale processes with heterogeneously catalysed gas-phase reactions; one process is endothermic and the other is exothermic. These evaluations are reported in sections 7 and 8.

The other applications in the short list were not selected, because of various reasons:
- lack of interest of end-users (10 processes),
- energy savings too low (3),
- development hurdles too high (3),
- company would not sign secrecy agreement (3),
- already considered as demonstration project (1).

7. EVALUATION OF AN ENDOTHERMIC PROCESS

This process is operated by a number of companies in the Netherlands and many more world-wide. The process is expected to grow in importance in the future. For this process, HEX reactors are much more compact than the conventional reactor, and offer a better temperature control. They are specially well suited for thermally coupling the endothermic and exothermic reactions, which occur in the process. The conventional process is well known to be energetically inefficient. Rough estimations reveal that energy savings in the order of 2 PJ/y can be expected in the Netherlands.

In a meeting with one company, the main conclusion was that although the use of HEX reactors looks very promising, especially for thermal coupling of the endothermic and exothermic reactions, the potential for large-scale processes is judged to be rather small. The main reason is that although HEX reactors are more technically advanced, they do not bring major step-change advantages over the heat-integrated designs already in use. Moreover, as most new plants are built in areas with low-cost feedstock, capital investment rather than energy efficiency or utility cost is of key importance for most producers. It is expected that HEX reactor innovations in this area will primarily come from smaller applications, where reactor size is of real importance, and where commercial breakthroughs can be expected in the near future. When HEX reactors are generally used and accepted for small-scale applications, it is likely that they will also be accepted and considered as proven technology for large-scale operation.

In the acceptance of HEX reactors for large-scale processes other design and operational issues also play a role:

- *Catalyst design*: In the conventional reactor catalyst pellets are used with a size of a few millimetres. This size is a compromise between a low pressure drop and sufficient mass- and heat transfer. For a HEX reactor these mm-size pellets are not suited for the small reactor channels. A solution can be to use smaller catalyst particles, but this will lead to a higher pressure drop, or the catalyst should be coated on the reactor channel walls. For both options the manufacture, loading and replacement of the catalyst is a challenging task, especially for large production capacities.
- *Reactor fouling*: Fouling is one of the main problems encountered in operation. The catalyst can suffer from coke formation and poisoning. With the smaller channels of a HEX reactor the risk of operability problems due to fouling is higher. Fouling can be reduced by using other feeds and by using an (adiabatic) pre-reactor. When the energy is supplied by utility (e.g. flue gas or by (catalytic) combustion of fuel) fouling of the reactor utility channels could also be a danger.
- *HEX reactor manufacture*: For this process high reaction temperatures are required and therefore the demands on the material of construction of a HEX reactor are high. The fabrication of large capacity HEX reactors will be a challenging task.
- *Economics*: This large-scale process is capital intensive. If capital cost (and total production cost) can be reduced significantly by application of a HEX reactor this will be a real incentive to the introduction of HEX reactors for large-scale operation.

8. EVALUATION OF AN EXOTHERMIC PROCESS

This process is a large-scale process with significant energy use in the Netherlands and world-wide. For this exothermic catalytic gas-phase reaction, state-of-the-art technology is stepwise adiabatic operation with direct or indirect cooling between two or more catalyst beds. Because the reaction is exothermic, the temperature rises with conversion. At the end of the first catalyst bed, the reaction rate becomes very low because the temperature approaches the equilibrium temperature. The effluent of the first catalyst bed is therefore cooled and reacted over a second bed to increase the conversion. The limited conversion necessitates a large recycle loop.

In principle, it should be possible to operate a HEX reactor along the optimum temperature profile over the whole conversion range. In the first part of the catalyst bed the maximum temperature is determined by the maximum allowable temperature for the catalyst and in the second part the reactor can work with a decreasing temperature profile, which is not possible with adiabatic operation. This allows operating the reactor at the maximum reaction rate over the whole reactor length. As a result, it should be possible to achieve a higher conversion per pass using the same amount of catalyst and space velocity. Considerable development work will be required to design a HEX reactor with the right characteristics for the optimum temperature profile. An important aspect will be the control of the unit.

In order to quantify the potential benefits, effort was put into the development of a reactor model based on thermodynamic and kinetic data from open literature. In a spreadsheet program a mass balance model was made of the reactor and the corresponding recycle loop, based on data obtained from the company concerned. However, the available kinetic data were found to be not good enough for the description of the reactor with reasonable accuracy. Therefore, calculations were performed using the black-box mass balance model only.

With this model, the effect of a higher conversion per pass (i.e. a reduction in the size of the recycle loop, or a higher production rate) could be quantified. However, the potential energy savings that can be achieved depend on the process configuration. To estimate the savings in full detail a redesign of the reactor section should be made. Nevertheless, an estimate was made of the maximum savings that can be obtained in reducing the size of the recycle loop, by means of Aspen Plus simulations. On this basis a saving of 4.2 PJ/y was estimated for the Netherlands.

Because the recycle loop is considerably smaller, there is also a considerable saving in capital cost. This means that even if the HEX reactor itself is more expensive than a conventional reactor, there can be an overall cost saving. An overall cost saving will be the main incentive for producers and process owners to start development work on HEX reactors.

9. CONCLUSIONS

9.1 Demonstration projects

Energy savings achievable by implementation of non-catalytic liquid-phase HEX reactors in the Netherlands are probably in the range 2-8 PJ/y.

Application to the selected polymerisation process is not very suitable for a short-term demonstration project. The potential energy savings are probably less than about 0.25 PJ/y (in NL).

Application to the selected oxidation process could make an interesting demonstration project. The potential energy savings are about 0.6 PJ/y for this plant, and there is a high repetition potential for other oxidation processes.

9.2 Broad inventory

Twenty-two HEX-reactor applications were identified, with total energy savings, which could amount to 20 PJ/y (in NL).

For the first selected process, energy savings of about 2 PJ/y might be expected (in NL), but the commercial potential is judged to be small.

For the second selected process, energy savings up to 4.2 PJ/y might be achieved (in NL), possibly together with cost savings. This application could be of interest for long-term development.

REFERENCE

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