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Synthesis and optimisation of a methanol process

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Abstract

In the present paper, a simulation model for a methanol process is proposed. The objective is to develop a model for flowsheet optimisation, which requires simple thermodynamic and unit operation models. Simplified thermodynamic models are combined with a more advanced model for the rate of reaction. The resulting model consists of a DAE-system. The model is compared with rigorous simulation results from Pro/II and good agreement is found. The process is optimised followed by heat integration and large differences in the operating economy of the plant can be observed as a result hereof. Moreover, the results indicate that optimisation of the process, heat integration, and utility system design cannot be regarded as separate tasks, but must be carried out simultaneously to find an optimal process.

Nomenclature

Symbols

A	Heat transfer area [m^2]
C	Cost [\$]
c_p	Specific heat capacity [$\text{kJ/kmole}\cdot\text{K}$]
E	Yearly earnings [\$]
F	Molar flow rate [kmole/s]
G	Mass flow flux [$\text{kg/m}^2\cdot\text{s}$]
ΔH_{rx}^0	Heat of reaction [kJ/kmole]
h_c	Convective heat transfer [$\text{kW/m}^2\cdot\text{K}$]
NPV	Net present value [\$]
r	Rate of reaction [$\text{mole / kg catalyst / s}$]
p	Pressure [bar]
T	Temperature [K]
U	Overall heat transfer coefficient [$\text{kW/m}^2\cdot\text{K}$]
W	Catalyst weight [kg]
y	Mole fraction [-]

Greek letters

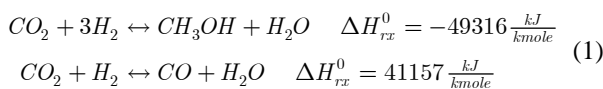
α	Relative volatility
θ	Heat exchanger approach temperature [K]
ρ	Density [kg/m^3]
ξ	Recovery coefficient

Subscripts

0	Inlet conditions, vapour pressure, reference temperature
1	Heat exchanger hot inlet
2	Heat exchanger hot outlet
b	Catalyst bulk
BM	Bare module
c	Catalyst solid
$cold$	Cold side of heat exchanger
GR	Grassroot
hot	Hot side of heat exchanger
k	k'th component
liq	Liquid fraction
n	Key component

Introduction

Methanol is one of the most important bulk chemicals and is synthesized in large-scale plants from syngas¹. The process includes production of syngas, conversion of syngas to methanol and purification of the crude methanol to the desired specification. The formation of methanol from syngas can be assumed to involve the following reactions.



In fig. 1 the core process for production of crude methanol is outlined. As the reactor only converts a limited amount of syngas into methanol, unreacted gas is either recycled or purged. Even though this is only one part of the entire process, the energy demands are large, both in terms of mechanical energy for compression of syngas and heating and cooling at various places.

¹ Syngas consists of H_2 , CO , and CO_2 .

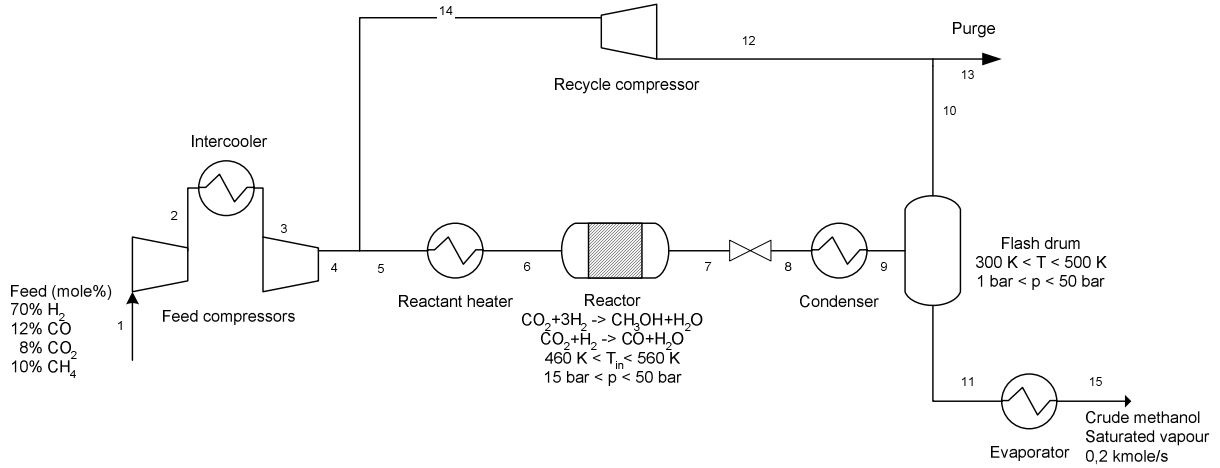


fig. 1 Conceptual flowsheet for production of crude methanol from syngas.

Optimisation of the process design is essential to obtain an economically feasible and competitive process. It is important to observe that in typical applications 80% of the capital cost will be fixed very early in the project in the conceptual design (Biegler *et al.* 97). Therefore, changes in the subsequent phases will only be able to save a maximum of 20% of the total capital cost.

The objective of this paper is to develop a model for a methanol process to be used, for flowsheet optimisation during the conceptual design phase. The model must be simple enough for flowsheet optimisation, while still capturing the correct behaviour of the unit operations. On the other hand, detailed models are not necessary during conceptual design, as they often require more data than what is available early in the project. The flowsheet optimisation is implemented in GAMS (Brooke *et al.* 98) and in order to evaluate the models they will be compared with commonly accepted rigorous models found in Pro/II by (Invensys 03).

Modelling

The model of the system includes a thermodynamic model of the chemical components, models of the individual unit operations and capital cost estimation. Since methanol plants are very large and operate continuously for more than 8000 hours per year, it is reasonable to use steady-state models for the flowsheet.

Thermodynamic models

The methanol reaction is a gas-phase reaction, implying that the components can be modelled as ideal gases, and for the temperature range in question it is reasonable to assume constant average specific heat capacities. A flash vessel is used for separation of crude methanol from unreacted syngas, this requires two-phase property prediction. The vapour pressures are calculated with the Antoine equation, and the heat of vaporisation are estimated from the Watson correlation

(Biegler *et al.* 97). All together this is a simple thermodynamic model, requiring only few equations.

Reactor model

The reactor is modelled as a packed-bed-reactor (PBR), where the syngas flows through a catalyst bed. For this study it is assumed that the reactor operates adiabatically. A homogenous model is used, even though it is a simplified approach; we consider it adequate for the purpose of conceptual design. The reaction rates for methanol are quite complex however especially since a wide range of operating conditions must be covered in order to avoid constraints on the optimisation. (Vanden Bussche and Froment 96) have proposed a rate expression that covers a range for $180^{\circ}\text{C} < T < 280^{\circ}\text{C}$ and $15 \text{ bar} < p < 50 \text{ bar}$. Following a couple of algebraic manipulations the rate equations are

$$r_{1,CH_3OH} = \frac{\left(k_d p_{CO_2} p_{H_2}^4 - \frac{k_d}{K_1^{eq}} p_{H_2} p_{H_2O} p_{CH_3OH} \right)}{\left(p_{H_2} + k_c p_{H_2O} + k_a p_{H_2}^{3/2} + k_b p_{H_2} p_{H_2O} \right)^3} \quad (2)$$

$$r_{2,H_2O} = \frac{k_e p_{CO_2} p_{H_2} - k_e K_3^{eq} p_{H_2O} p_{CO}}{p_{H_2} + k_c p_{H_2O} + k_a p_{H_2}^{3/2} + k_b p_{H_2} p_{H_2O}}$$

The kinetic constants k_1, \dots, k_7 are given in the appendix. The mole balance for each species in the PBR are as follows:

$$\begin{aligned} \frac{dF_{CO}}{dW} &= r_{2,H_2O} \\ \frac{dF_{H_2O}}{dW} &= r_{1,CH_3OH} + r_{2,H_2O} \\ \frac{dF_{CH_3OH}}{dW} &= r_{CH_3OH} \\ \frac{dF_{H_2}}{dW} &= -3r_{1,CH_3OH} - r_{2,H_2O} \\ \frac{dF_{CO_2}}{dW} &= -r_{1,CH_3OH} - r_{2,H_2O} \end{aligned} \quad (3)$$

The energy equation for an adiabatic PBR with q reactions and m species can be formulated as:

$$\frac{dT}{dW} = \frac{\sum_{i=1}^q (-r_{ij}) [-\Delta H_{RXij}(T)]}{\sum_{j=1}^m F_j c_{p,j}} \quad (4)$$

Conservation of momentum in a packed bed is modelled by the Ergun equation, (Fogler 99). Assuming an average density throughout the reactor, the expression can be reformulated into an algebraic equation.

$$\frac{1}{2}(p_{out}^2 - p_{in}^2) = -\frac{\alpha}{2} \frac{T_{in} + T_{out}}{2T_0} p_0^2 \frac{F_{t,in} + F_{t,out}}{2F_{t0}} W_{total} \quad (5)$$

It must be noted that the assumption of constant density does not hold in reality, but the simplified equation will provide an estimate for the pressure drop through the reactor.

Flash calculations

In the flash calculation the simplified model proposed by (Biegler *et al.* 97) is used. A key component is selected from which the recovery of the non-key components can be calculated as:

$$\xi_k = \frac{\alpha_{k,n} \xi_n}{1 + (\alpha_{k,n} - 1) \xi_n} \quad ; \quad \alpha_{k,n} = \frac{p_0^k}{p_0^n} \quad (6)$$

In addition, the bubble-point equation must be fulfilled:

$$p = \sum_i y_{liq,i} p_0^i \quad (7)$$

The flash is considered adiabatic, and hence the outlet temperature is equivalent to the inlet. The pressure drop through the flash vessel is assumed zero.

Heat exchangers

The heat transfer in the heat exchangers are normally based on the logarithmic mean temperature difference, but this method fails if the flow capacity rates for the two sides of the heat exchanger are identical, and besides the method is numerically unstable. Therefore, the following approximation proposed by (Paterson 84) is used.

$$\dot{Q} = UA \Delta T_{lm} \approx UA \left(\frac{2}{3} \sqrt{\theta_1 \theta_2} + \frac{1}{6} (\theta_1 + \theta_2) \right) \quad (8)$$

$$\frac{1}{U} \approx \frac{1}{h_{c,hot}} + \frac{1}{h_{c,cold}}$$

The convective heat transfer coefficients are estimated from (Peters *et al.* 03); while only an estimate, this eliminates the need for a detailed heat exchanger design.

Sizing and cost estimation

Capital costs are approximated by the methods described in (Turton *et al.* 98). The cost equations cover a very large range, which makes them highly non-linear. Therefore, a set of equations have been derived to cover the specific area of application considered in this paper, see the appendix. The grassroot cost² of a plant is

$$C_{GR} = 1.18 \sum_{i=1}^{Units} C_{BM,i}^0 + 0.35 \sum_{i=1}^{Units} C_{BM,i} \quad (9)$$

The bare module cost at base conditions (C_{BM}^0) are calculated as the bare module cost (C_{CM}^0) at ambient pressure and carbon steel construction. The sizing of the equipment are carried out along the following guidelines

- Pressure vessels are assumed to have a length to diameter ratio of four.
- The volume of the flash vessel is twice the volume needed for a liquid hold up time of 5 minutes.
- All components are constructed using stainless steel.

Finally, it is chosen to use the Net Present Value as the objective function for the optimisation problem

$$NPV = -C_{GR} + \sum_{n=1}^{10} \frac{E_n}{(1+i)^n} \quad (10)$$

Solution procedure

Given the models outlined in the previous section, it is possible to optimise the flowsheet. When the flow sheet is optimised, and the temperature levels are determined heat integration is carried out. This is in line with the hierarchical design method proposed by (Douglas 88), where the most important part of the process is designed first.

All the unit operation models along with thermodynamic models and kinetic models have been implemented into a database. Given a flowsheet structure provided through the user interface a GAMS-datafile is generated and sent to GAMS. The problem is solved in GAMS and the results returned to the user-interface. Subsequently the results can be used as input to the Pro/II simulation program for a more rigorous simulation.

Solution of ODEs

The reactor model results in a number of ODEs that need to be solved, and since they cannot be solved

² Grassroot cost is a common term in chemical engineering referring to a completely new facility, i.e. the construction is started on a grass field.

analytically, a numerical method must be applied. Several methods are available, e.g. the well-known Runge-Kutta method. However, for optimisation we need the problem transformed into a number of algebraic equations, and for this purpose the method of orthogonal collocation points on finite elements (OCFE) have been successfully applied in a number of studies, e.g. (Biegler *et al.* 02). In fig. 2 two different meshes (3 and 5 elements, both with 2 collocation points) are com-

pared to the solution obtained by a standard ODE-solver. Three elements are too few, with large deviations from the standard ODE-solver. Five elements provide a far better solution; there still are some discrepancies, but nevertheless the outlet conditions match very well. In relation to the rest of the system, the output from the reactor is of primary interest rather than the internal states, and therefore five elements are considered sufficient for this purpose.

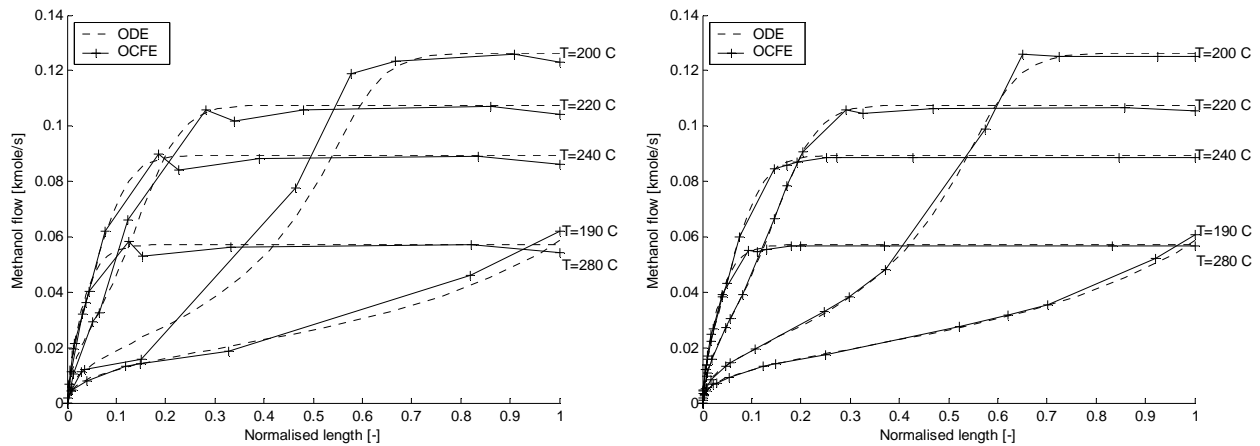


fig. 2 Simulation of methanol formation with different reactor inlet temperatures. To the left three elements have been used and to the right five elements have been used. The dotted line are the solution by a traditional ODE-solver.

Heat integration

The synthesis of the heat exchanger network is based on the method described by (Yee *et al.* 90), where a super structure for the heat exchanger network is proposed. The cost estimation method used in this paper is slightly different however, so the method has been changed to fit into the present work.

Results

The process from the optimisation can briefly be summarised as:

- Reactor inlet conditions: $T=473$ K, $p=45.5$ bar
- Flash conditions: $T=321$ K, $p=44.7$ bar
- Purge rate: 5%

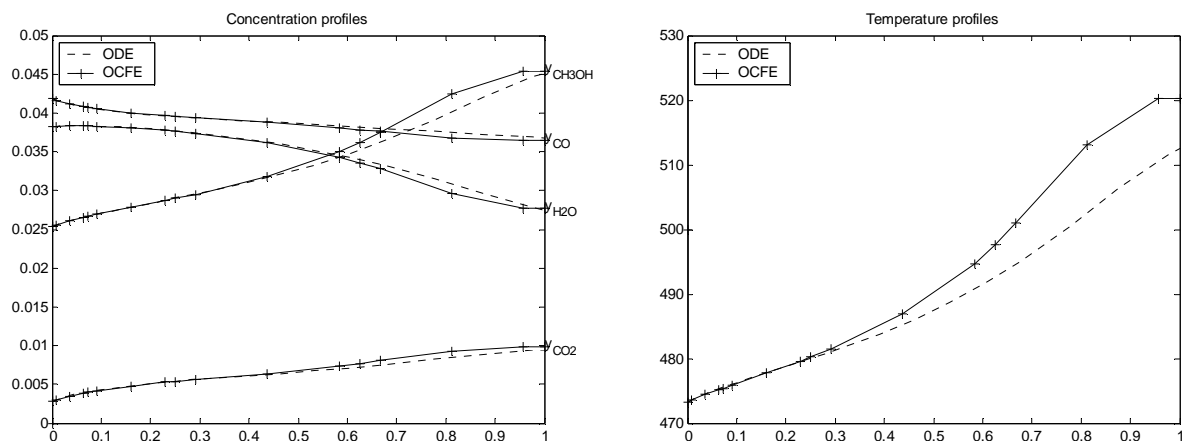


fig. 3 Comparison of reactor model in GAMS and a rigorous model. The GAMS model has calculated the results at the collocation points (marked with crosshairs), while the rigorous model is represented by the continuous curves.

Comparison with rigorous process model

The optimisation has been carried out with simplified models, and for verification the result is compared with rigorous models from Pro/II (Invensys 03), see fig. 3. It

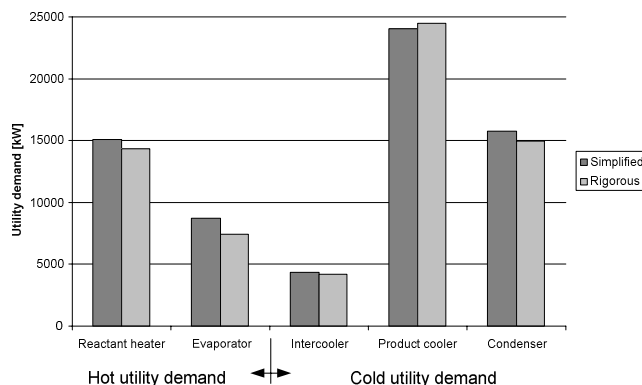


fig. 4 Comparison of the utility demand calculated by Pro/II and the simplified models

The utility demand calculated by the simplified models agrees quite well with the rigorous models. It is considered adequate for flowsheet optimisation. The flash model shows some deviations regarding the fraction of light components in the liquid fraction. Still the level of the major liquid components (methanol and water) agrees very well, implying that the deviations only have very limited impact on the result.

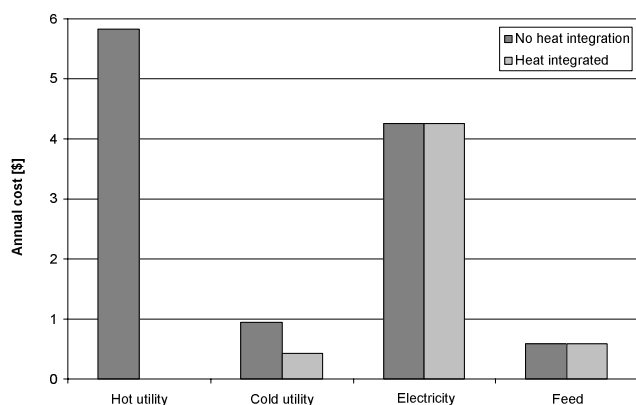


fig. 6 Annual operating costs both with and without heat integration

As the hot utility can be eliminated, it will have a major impact on the optimisation of the core process, as the annual operating cost would be significantly reduced. It is important to recognise the high impact from the operating costs, especially hot utility and electricity, making it necessary for the optimisation of heat exchanger network and utility system to be included at a very early stage. Otherwise, there is a sig-

nificant risk that the overall solution ends up being suboptimal. In a future paper a more integrated approach for the design will be set forth, but so far it has only been recognised that the problem exists.

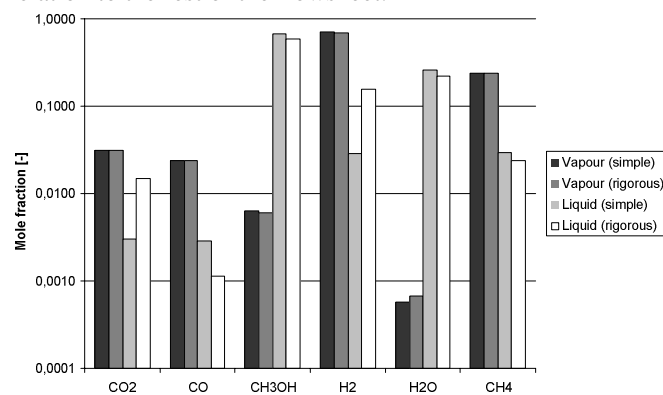


fig. 5 Comparison of the flash calculation by Pro/II and the simplified calculations. Note the use of a logarithmic scale.

Discussion of optimisation results

Considering the yearly operating costs, it is very interesting to notice that steam and electricity accounts for more than 90% of total, fig. 6. On the other hand, the feed and cold utility cost is almost negligible in this context. The consequence is that the hot utility and electricity has major influence on the overall economy of the plant, and thereby on the optimisation problem. If heat integration is applied to the process the need for hot utility can be eliminated, see fig. 6 and fig. 7.

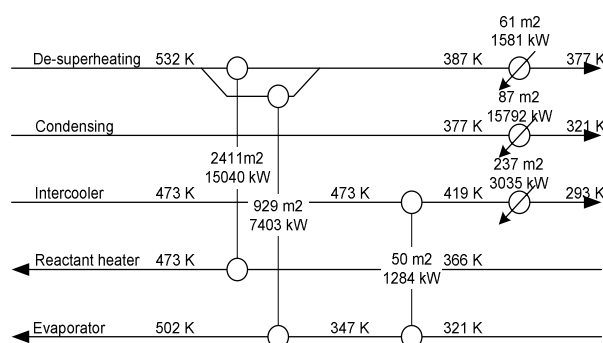


fig. 7 Heat exchanger network for heat integrated plant. Please note that the condenser is split into a de-superheating section and a condensing section

Conclusion

In the present paper, a simulation model for a methanol process has been proposed, which can be used for flowsheet optimisation purposes. The model combines simplified thermodynamic models, with a more advanced model for the rate of reaction. The resulting model consists of a DAE-system discretising the ODEs with orthogonal collocation points on finite elements an algebraic equation system is obtained. The model at the optimum point is compared with rigorous models from Pro/II and there is a good agreement between the results.

A closer look at the optimisation results shows that there is a very large potential for energy and economic saving, which will have a major influence on the plants economy. It must be concluded that a sequential design procedure, in which the heat integration and utility system design is done after optimisation of the process probably leads to sub optimal solutions. In a future paper, a comprehensive design method for simultaneous optimisation of process, heat and utility supply will be presented.

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Appendix

Kinetic data

The constants for the rate equations are given in table 1.

table 1 Parameter values in the kinetic model.
T is given in [K] and R_g is 8.315 kJ/kmole-K

$k = A \exp(B / (R_g T))$	A	B
k_a [bar ^{-0.5}]	0.499	17,197
k_b [bar ⁻¹]	6.62e-11	124,119
k_c [-]	3,453.38	0
k_d [mole / (kg-s-bar ²)]	1.07	36,696
k_e [mole / (kg-s-bar)]	1.22e10	-94,765
k_d / K_1^{eq} [mole / (kg-s)]	4.182e10	-22,005
$k_e K_3^{eq}$ [mole / (kg-s-bar)]	1.142e8	-55,078

Cost estimation

The cost estimation functions used in this article are summarised in table 2 and table 3.

table 2 Cost estimation functions for major process equipment

Equipment	Purchased cost [\$]	Pressure correction [-]	Bare module cost [\$]	Range
Pressure vessel ³	$C_p = 3254.9V^{0.5457}$	$F_p = 0.0369p + 1.3644$	$C_{BM}^0 = C_p (1.62 + 1.47F_M F_p)$	0.1-200 m ³
Compressors ⁴	$C_p = 987.42W^{0.9542}$	-	$C_{BM}^0 = F_M C_p$	100-8000 kW
Heat exchangers	$C_p = 719.15A^{0.6518}$	$F_p = 0.7884p^{0.0988}$	$C_{BM}^0 = C_p (1.8 + 1.5F_M F_p)$	50-900 m ²

table 3 Material factors (F_M)

Equipment	Carbon steel	Stainless steel	Nickel Alloy
Pressure vessel	1.0	4.0	9.8
Compressors	2.5	6.3	13.0
Heat exchangers	1.0	3.0	3.8

³ Only applicable for a length:diameter ratio of 4

⁴ Only applicable for centrifugal compressors