CHAPTER II
LITERATURE REVIEW

LITERATURE REVIEW

This chapter reviews the literature work and research undertaken in reactive distillation to date. Extensive survey of literature was done in the libraries of Sant Gadge Baba Amravati University, Amravati, UICT Mumbai, NCL Pune. Also a substantial amount of literature and research papers were downloaded through the online digital library DELNET.

Here a brief abstract of the papers published related to Reactive distillation technology with relevance to this thesis are mentioned. It is worth noting that though a quantum of work has been undertaken in this Rd technology certain aspects still needs to be explored.
1. Comparative control study of ideal and methyl acetate reactive distillation

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The control of an ideal reactive distillation column is compared with that of a similar, but somewhat different, real chemical system, the production of methyl acetate. Similarities and differences are observed. Three control structures are evaluated for both systems. A control structure with one internal composition controller and one temperature controller provides effect control of both systems for both high and moderate conversion designs. A two-temperature control structure is effective when the system is overdesigned in terms of number of reactive trays, holdup and/or catalyst load. Direct control of product purity for the high-conversion/high-purity design is difficult because of system nonlinearity and interaction. Tray temperature control avoids the nonlinearity problem.

2. Design of Reactive Distillation

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This paper presents an overview of the progress of a three-year project "Reactive distillation" initiated by SUSTECH and supported by EU and the main results. Reactive distillation (RD) is a process that combines reaction and distillation into one step. Though the advantages of RD are well documented it's commercial applications are still few. Reasons to this are the complexity of the process, lack of knowledge to design these systems, need for improved software tools to evaluate and design RD, and limited number of suitable catalyst and equipment to place catalyst inside the column. To overcome these obstacles a three-year project "Reactive distillation" initiated by SUSTECH and supported by EU in the frame of the BriteEuram III project.
program was formed. The consortium consists of the companies Neste Oyj (Finland, Co-ordinator), BP Chemicals (Great Britain), Hoechst (Germany), BASF (Germany), Snamprogetti (Italy), and universities of Clausthal (Germany), Dortmund (Germany), Aston (Great Britain), Bath (Great Britain) and Helsinki University of Technology (Finland). This paper presents an overview of the progress of the project and the main results.

3. Distillation column with reactive pump arounds: an alternative to reactive distillation

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Their study presented reveals the potential, and limitations, of the side-reactor concept for use as an alternative to RD technology. The hardware design of reactive distillation (RD) columns pose severe challenges with respect to the choice and design of the hardware; the requirements of reaction (i.e. high liquid or catalyst holdup) is not in consonance with the requirement of separation (high interfacial area). In this paper, we examine an alternative to the RD concept, namely a distillation column networked with a number of side (external) reactors. If each distillation stage is linked to a side reactor, the performance of the RD column is matched exactly. From a practical point of view, it is desirable to reduce the number of side reactors to below, say, six. The precise location of the chosen number of side reactors and the manner in which the liquid draw-offs and reactor effluent re-entry to the distillation column needs to be chosen carefully. We have developed an algorithm to determine an optimum configuration of the side-reactor concept in order to maximise conversion. For the case study of methyl acetate production, we see that it is possible to match the conversion level of an RD column by appropriate choice of the number of side reactors and the pump around ratio. The higher the conversion target the larger the number of side reactors and pump around ratios. For modest conversion levels, say <90%, even a 3-side-reactor configuration will be able to match the performance of the RD column.
4. Effects of feed tray locations to the design of reactive distillation and its implication to control
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Explored the effects of feed locations to the design of reactive distillation. In this work, ideal reactive distillation systems are used to illustrate the advantage of feed trays optimization in design and control. Process parameters such as relative volatilities between reactants, relative volatilities between products, column pressure, activation energies, and pre-exponential factors are varied to seek possible generalization. For all systems studied, the percentage of energy saving ranges from 6% to 47%, and this is obtained by simply rearranging the feed locations. Finally, the idea of optimal feed trays is extended to the operation/control of reactive distillation systems. First, steady state analysis is carried out to find the optimal feed trays as measurable load variable varies. Then, a control structure is proposed to rearrange the feeds as the disturbance comes into the system. The results indicate that, again, substantial energy can be saved by feed rearrangement via the coordinated control structure.

5. Kinetic transition in excited-state reversible reactions
Noam Agmon, Irina V. Gopich The Fritz Haber Research Center, Department of Physical Chemistry, The Hebrew University, Jerusalem 91904, Israel

Demonstrated that reversible reactions occurring in the excited electronic state undergo a 'kinetic transition' as a function of the difference in excited-state decay rates. This conclusion follows from a remarkably accurate approximate solution obtained for the kinetics of diffusion-influenced reversible geminate dissociation reactions in solution, which becomes exact at long times. q1999 Elsevier Science B.V.

6. Mass transfer in osmotic membrane distillation of phycoeyanin colorant and sweet-lime juice
B. Ravindra Babu, N.K. Rastogi*, K.S.M.S. Raghavarao Department of Food Engineering, Central Food Technological Research Institute, Mysore 570020, Karnataka, India
Osmotic membrane distillation is a novel membrane process for the removal of water from dilute aqueous solutions, such as liquid foods or natural colors, concentrating them, while retaining the organoleptic and nutritional properties. The effect of various process parameters, such as concentration (2–10 m) and flow rate (25–100 ml min⁻¹) of feed and osmotic agent on the transmembrane flux was evaluated in case of phycocyanin and sweet-lime juice.


In this contribution, the benefits of using dynamic models of different complexity and size for process design, optimal operation and control of catalytic distillation (CD) processes are discussed for the case study of the heterogeneously catalysed reactive distillation (RD) of methyl acetate. Dynamic reactive distillation experiments at pilot plant scale were performed using the catalytic structured packing MULTIPAK. A dynamic rate-based model were developed which contains hydrodynamic effects as liquid holdup, liquid backmixing and pressure drop as well as reaction kinetics and which describes the process behaviour accurately. For offline and online optimisation and control, reduced order and simplified models were applied. A systematic control structure selection and controller design studies for the experimental column were conducted. The linear controller shows good performance over a wide range of operating conditions.

8. Modeling and simulation of reactive distillation columns using computer algebra Marcelo F. Alfradique, Marcelo Castier *Escola de Química, Universidade Federal do Rio de Janeiro, Caixa Postal 68542, Rio de Janeiro, RJ 21949-900, Brazil

This work presents an extension of a computer algebra (CA) program, Thermath, originally developed for the automatic implementation of physical property calculations, to generate computer codes in Fortran for the
Optimization of Design & Operation in Reactive Distillation

simulation of steady-state reactive distillation columns. The adopted procedure requires the simultaneous solution, using the Newton–Raphson method, of mass and energy balances, phase equilibrium equations, chemical equilibrium or rates of reaction equations and an additional equation needed to match the number of degrees of freedom. The Thermath program was used to obtain Fortran subroutines that implement these equations and their derivatives with respect to the process variables and the equation of state and/or excess Gibbs free energy model used in the simulation. The results are in excellent agreement with those available in the literature. By using Thermath, it was possible to reduce the time and effort needed to implement the mathematical models of multistage reaction–separation equipment.

9. Modelling reactive distillation R. Taylor1,*, R. Krishna#, • Department of Chemical Engineering, Clarkson University, Potsdam, NY 13699-5705, USA "Department of Chemical Technology, University of Twente, 7500 AE Enschede, The Netherlands #Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

The design and operation issues for reactive distillation systems are considerably more complex than those involved for either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between vapor–liquid equilibrium, vapor–liquid mass transfer, intra-catalyst dilution (for heterogeneously catalysed processes) and chemical kinetics. Such interactions have been shown to lead to the phenomenon of multiple steady-states and complex dynamics, which have been verified in experimental laboratory and pilot plant units. We trace the development of models that have been used for design of reactive distillation columns and suggest future research directions.

10. Packings for fixed bed reactors and reactive distillation C. Miller*, G. Kaibel BASF AG, GCE/D, Carl-Bosch-Strasse 38, M300 D-67056 Ludwigshafen, Germany

Trickle-bed reactors in which gas and liquid cocurrently flow downward
through a packed catalyst bed are common in the chemical and petroleum industries. The recent development of more active catalysts is pushing commercial operations to higher flow rates, towards the pulsing flow regime and to smaller catalyst particles. A new development of BASF tries to improve trickle-bed reactors by installing corrugated distillation packings within the reactor and pouring catalyst particles into the packing. By using a packing in a reactor a mechanical support to the catalyst is provided, the pressure drop is reduced, and higher liquid-throughputs are possible. The packing also leads to an onset of pulsing at higher liquid and gas loads. Hydrodynamic studies of trickle-bed reactors with and without packings were conducted over a series of catalysts. The measurements include pressure drop, loading capacity and abrasion. The experiments were conducted at high gas and liquid flow rates and at low gas and liquid flow rates. The hydrodynamic regimes have been characterized. For the application of this system to catalytic distillation a new kind of packing, the so-called multi-channel packing, was developed to obtain higher gas throughputs. By simply alternating packings with high and low specific surface areas the gas throughput can be increased significantly. Hydrodynamic studies were conducted for packings with different catalyst contents. The measurements include pressure drop, flooding point, liquid hold-up, and residence time.

11. Phase equilibria and excess properties for binary systems in reactive distillation processes Part I. Methyl acetate synthesis

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Isothermal vapor-liquid equilibrium (VLE) and excess enthalpy (HE) data were measured for binary systems required for the design of reactive distillation processes for the methyl acetate production. The isothermal P-x data were measured with the help of a computer-operated static apparatus. A commercial isothermal flow calorimeter was used for the determination of the heats of mixing. Temperature-dependent interaction
through a packed catalyst bed are common in the chemical and petroleum industries. The recent development of more active catalysts is pushing commercial operations to higher flow rates, towards the pulsing flow regime and to smaller catalyst particles. A new development of BASF tries to improve trickle-bed reactors by installing corrugated distillation packings within the reactor and pouring catalyst particles into the packing. By using a packing in a reactor a mechanical support to the catalyst is provided, the pressure drop is reduced, and higher liquid-throughputs are possible. The packing also leads to an onset of pulsing at higher liquid and gas loads. Hydrodynamic studies of trickle-bed reactors with and without packings were conducted over a series of catalysts. The measurements include pressure drop, loading capacity and abrasion. The experiments were conducted at high gas and liquid flow rates and at low gas and liquid flow rates. The hydrodynamic regimes have been characterized. For the application of this system to catalytic distillation a new kind of packing, the so-called multi-channel packing, was developed to obtain higher gas throughputs. By simply alternating packings with high and low specific surface areas the gas throughput can be increased significantly. Hydrodynamic studies were conducted for packings with different catalyst contents. The measurements include pressure drop, flooding point, liquid hold-up, and residence time.

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parameters for the UNIQUAC model were fitted simultaneously to the experimental data from this work and other authors.

12. Reactive and catalytic distillation from an industrial perspective

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Reactive and catalytic distillation has attracted growing interest, both in industry and in scientific research. This contribution gives an overview of the tools that are available today and the methods that have now been introduced into the industrial practice in a large chemical company. A process synthesis gives good qualitative reference points. Simulation tools have been developed which are mainly equilibrium-based. However, further steps are necessary on the way to implementation in an industrial plant. The scale-up from the miniplant used for the experimental validation of a new process is well known for conventional distillation, but complicated by several facts for reactive distillation specifically in the case of heterogeneous catalysis. To overcome these problems reference plant experience on an industrial scale is necessary or if not available will require future research. Other options both for homogeneous and heterogeneous catalysis are possible and will be discussed in the contribution. Attention is drawn to the fact that a combination of reaction and distillation does not necessarily have to be operated in a column. For slower reactions a broad range of equipment not necessarily containing columns can be used.

13. Reactive distillation for methyl acetate production

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Describe a hierarchy of methods, models, and calculation techniques that support the design of reactive distillation columns. The models require increasingly sophisticated data needs as the hierarchy is implemented. The approach is illustrated for the production of methyl acetate because of its
commercial importance, and because of the availability of adequate published data for comparison. In the limit of reaction and phase equilibrium, we show (1) the existence of both a minimum and a maximum reflux, (2) there is a narrow range of reflux ratios that will produce high conversions and high purity methyl acetate, and (3) the existence of multiple steady states throughout the entire range of feasible reflux ratios. For finite rates of reaction, we find (4) that the desired product compositions are feasible over a wide range of reaction rates, up to and including reaction equilibrium, and (5) that multiple steady states do not occur over the range of realistic reflux ratios, but they are found at high reflux ratios outside the range of normal operation. Our calculations are in good agreement with experimental results reported by Bessling et al., *Chemical Engineering*

14. **Scale-up of reactive distillation columns with catalytic packings**
Achim Hoffmann*, Christoph Noeres, Andrzej Górak Chair of Fluid Separation Processes, Department of Biochemical and Chemical Engineering (BCE), Dortmund University, 44221 Dortmund, Germany

The scale-up of reactive distillation columns with catalytic packings requires the knowledge of reaction kinetics, phase equilibrium and packing characteristics. Therefore, pressure drop, liquid holdup and separation efficiency have been determined for the catalytic packing MULTIPAK®. A new hydrodynamic model that describes the countercurrent gas-liquid flow for the whole loading range and considers the influence of the column diameter has been implemented into a rate-based column model. Simulation results for the methyl acetate synthesis are compared with pilot plant experiments that cover a wide range of different process conditions. The experiments are in good agreement with the simulation results and confirm the applicability of the modelling approach for reactive distillation processes with catalytic packings.

15. **Studies on the thermokinetics of reversible reactions** Jing-Song Liu *, Xian-Cheng Zeng, An-Min Tian and Yu Deng Department of Chemistry,
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Some new mathematical models of reversible reaction kinetics, using which both rate constants and equilibrium constants can be calculated simultaneously, are suggested and a reduced-extent method for studies of thermokinetics of reversible reactions is proposed. In the light of these models, two reversible reaction systems have been studied using a conduction calorimeter. The rate constants and equilibrium constants calculated are in fair agreement with those given in the literature.

16. Systematic structure generation for reactive distillation processes S. Giessler a, R.Y. Danilov b, R.Y. Pisarenko b, L.A. Serafimov b, S. Hasebe a, I. Hashimoto a a Department of Chemical Engineering, Kyoto University, Kyoto 606-8501, Japan b Lomonosov Academy of Fine Chemical Technology, 117571 Vernadskogo prospect, 86 Moscow, Russia

This paper proposes a systematic structure generation method for reactive distillation processes. When a feed composition to the process is given, the maximum degree of conversion and product compositions of the reactive distillation column are calculated by using the method called Static Analysis (SA). In order to derive the results, the SA uses only the information about the physicochemical properties of the reaction mixture and a selected feed composition. From the results obtained by the SA, the entire feed composition region is classified into several subregions, each of which has different product configurations. Then, a specific process structure consisting of two or three columns is generated for each of the feed subregions. Finally, the design parameters of the columns and the operating conditions are determined by a process simulator. The proposed method is applied to three example problems: the production of MTBE, the esterification of methanol and acetic acid, and the hydrolysis of methyl acetate. The results show that many different feasible structures are enumerated systematically, and that most of the infeasible structures can be eliminated before precise simulations are executed. In the SA, unrealistic assumptions such as infinite flow rate in the column are introduced to simplify the analysis. However, for the above-mentioned examples a good agreement between the results of the SA and
those obtained by precise simulations is achieved. Thus, it can be concluded that the results obtained by using the SA are reliable and can be widely used to generate feasible structures of RD processes.

17. Thermo-kinetic time-parameter method for reversible reactions
Yong Chen, Hai-Dong Wang, Xian-Cheng Zeng*Department of Chemistry, Sichuan University, Chengdu 610064, PR China

According to the theoretical basis of thermo-kinetics, a novel thermo-kinetic research method, the time-parameter method for reversible reactions, has been proposed in this paper. The rate constants of forward and backward reactions and equilibrium constant can be calculated from the same thermoanalytical curve simultaneously with this method. In order to test the validity of this method, the proton-transfer reactions of nitroethane with ammonia at 15 and 258C, and with Tris at 15 and 308C have been studied, respectively. The results of rate constants and equilibrium constants calculated with this method are inagreement with those in the literature. Therefore, the time-parameter method for the reversible reaction is believed to be correct.

18. Towards further internal heat integration in design of reactive distillation columns—part I: The design principle
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The thermodynamic efficiency of a reactive distillation column involving reactions with a highly thermal effect could sometimes be improved substantially through seeking further internal heat integration between the reaction operation and separation operation. Prudent arrangement of the reactive section and deliberate determination of feed location are the two effective methods that can complement internal heat
Integration within a reactive distillation column. The reactive section is suggested to properly superimpose onto both the stripping section for exothermic reactions and the rectifying section for endothermic reactions. Feed location should be determined so that the effect of internal heat integration can be maximized between the reaction and separation operations. Two reactive distillation systems, involving a highly exothermic reaction and a highly endothermic one, are employed to evaluate the proposed design philosophy and the results obtained confirm its feasibility and effectiveness. In addition, sensitivity analysis is conducted with respect to the amount of catalyst employed, relative volatilities of reacting mixtures, and thermal condition of feeds. The applicability and potentials of the design principle proposed are highlighted.

19. Transesterification processes by combination of reactive distillation and pervaporation Sven Steinigeweg, Jürgen Gmehling, Carl-von-Ossietzky-University of Oldenburg, Chair of Industrial Chemistry, 24 May 2003
The development of a reactive distillation process for the production of n-butyl acetate by transesterification of methyl acetate with n-butanol is presented. Thermodynamic aspects of the quaternary system n-butyl acetate–n-butanol–methyl acetate–methanol are discussed and UNIQUAC interaction parameters derived using the Dortmund Data Bank (DDB) are given. The reaction kinetics of the heterogeneously by a strongly acidic ion-exchange resin (Amberlyst 15) catalyzed reaction has been investigated and the kinetic constants for a pseudohomogeneous kinetic model are presented. Pervaporation experiments using Pervap 2255 membranes have been conducted for the separation of the methanol–methyl acetate binary mixture which forms the distillate stream of the reactive distillation column. Reactive distillation experiments have been performed using the structured catalytic packings Katapak-S (Sulzer Chemtech) and Katapak-SP (type SP 11, Sulzer Chemtech). Important operating conditions (reflux ratio, total feed rate) have been varied experimentally. The experimental results are presented in comparison with simulation results. An equilibrium stage model for the
modeling of the distillation is capable of describing the composition profiles quantitatively. Finally, a new process, combining reactive distillation with pervaporation, has been developed and investigated by means of simulation studies. It has been shown that the combination of reactive distillation with pervaporation is favorable since conversions close to 100% can be obtained with a reasonable size of the reactive section.


In this contribution, the benefits of using dynamic models of different complexity and size for process design, optimal operation and control of catalytic distillation (CD) processes are discussed for the case study of the heterogeneously catalysed reactive distillation (RD) of methyl acetate. Dynamic reactive distillation experiments at pilot plant scale were performed using the catalytic structured packing MULTIPAK. A dynamic rate-based model were developed which contains hydrodynamic effects as liquid holdup, liquid backmixing and pressure drop as well as reaction kinetics and which describes the process behaviour accurately. For offline and online optimisation and control, reduced order and simplified models were applied. A systematic control structure selection and controller design studies for the experimental column were conducted. The linear controller shows good performance over a wide range of operating conditions.

21. Optimal reactor structures for exothermic reversible Reactions with complex kinetics F. Hopley, D. Glasser AND D. Hildebrandt Department of Chemical Engineering, University of the Witwatersrand, Private Bag 3, WITS, 2050, South Africa

Exothermic reversible reactions are industrially very significant. Previous work has looked at finding the Attainable Region for elementary kinetics and in this paper we extend the work to find optimal reactors for more complex kinetics. Using these results we show how the complexity of
the kinetics affects the nature of the optimal reactor. In particular it is found that the optimal reactor structure includes a novel element, namely two parallel structures, the first of which has preheating followed by the following reactors connected in series: a plug flow reactor, CSTR, plug flow reactor and finally differential side stream reactor, while the second structure is a plug flow reactor. The side streams in the DSR are taken from various points along the plug flow reactor making up the second parallel structure. Furthermore, it is also shown that in order to satisfy optimality conditions on the boundary of the Attainable Region, the rate of reaction of the material in the side stream to the DSR and that in the DSR at the point where the side stream is added must be equal. The equations describing the DSR operation as well as the conditions describing the operation of the other reactors in the optimal reactor structure are given.

22. Scale-up of reactive distillation columns with catalytic packings

Achim Hoffmann*, Christoph Noeres, Andrzej Góra
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23. Systematic structure generation for reactive distillation processes S. Giessler a, R.Y. Danilov b, R.Y. Pisarenko b, L.A. Serafimov b, S. Hasebe a,*,I. Hashimoto a a Department of Chemical Engineering, Kyoto University, Kyoto 606-8501, Japan b Lomonosov Academy of Fine Chemical Technology, 117571 Vernadskogo prospect, 86 Moscow, Russia

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24. Multi-fields synergy in the process of reactive distillation coupled with membrane separation Huajun Wang, Bolun Yang *, Jiang Wu, Guosheng Zhao, Xianhu Tao Department of Chemical Engineering, Xian Jiaotong University, Xian, Shaanxi, China

A new method for analyzing reactive distillation coupled with membrane separation system was proposed with the viewpoint of
nonequilibrium thermodynamics and the phenomenological theory. The synthesis of ethyl tert-butyl ether was chosen as a model system. The synergy of multi-fields such as temperature, concentration and chemical potential in this combined process was discussed; the relationship of each vector within a field was investigated by considering both of Soret effect and Dufour effect. The equations of mass and heat fluxes were established and the coefficients for both of them were obtained with the condition of the synergy in multi-fields. It can be known from the research results that the mass and heat transfer rate were increased or decreased with the synergy of multi-fields; the direction of transfer was also changed by the effect of synergy of multi-fields. From the viewpoint of field synergy, the model of non-equilibrium stage for the reactive distillation coupled with membrane separation was developed. The model incorporated complex reaction kinetics, vapor–liquid non-idealities, distillation and pervaporation process. The rapid solution for this model can be obtained by Newton–Raphson method. Simulation results are in good agreements with the experimental results.

25. Global optimization of reactive distillation networks using IDEAS
Jeremy F. Burri, Vasilios I. Manousiouthakis*,† Chemical Engineering Department, University of California at Los Angeles, Los Angeles, CA 90095, USA
In this work, we present a methodology for the global optimization of reactive distillation (RD) networks, through the Infinite DimEnsionAl State-space (IDEAS) approach. Within the IDEAS framework, network synthesis is formulated as an infinite dimensional linear optimization problem. The IDEAS conceptual framework is realized through solution of a series of finite dimensional linear programs whose optimum values converge to the infinite program’s infimum. The proposed optimal design methodology is demonstrated on a case study involving reactive distillation-based synthesis of methyl tert-butyl ether (MTBE) from isobutene and methanol.