Study on Suspension Catalytic Distillation for Synthesis of Linear Alkylbenzene

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An extensive study is presented of linear alkylbenzene (LAB) synthesis by suspension catalytic distillation (SCD) with supported PW heteropoly acid catalyst. SCD is a new development of catalytic distillation in which the catalyst particles are suspended in the liquid and recirculated through a separator equipped without the column, while in traditional catalytic distillation the catalyst is generally fixed in the column. SCD has shown more advantageous characteristics for LAB synthesis in an exploratory experiment of bench scale. A completely rate-based simulator RaCOLUMN for SCD process is developed, and as a case study used to simulate the profiles of concentrations, temperatures and other important process variables in SCD for LAB synthesis. Simulation results can agree well with the experimental data obtained in a stainless steel tray column with 23 sieve trays. It is found that, although the benzene/olefin ratio in the feed entering into the SCD column is very small, the concentration of benzene in the reaction section of the SCD column could maintain a large value because of the distillation effect, which is favorable to prohibit side reactions in alkylation process. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 845–853, 2005
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Introduction

Linear alkylbenzene (LAB) is a basic and important petrochemical intermediate for manufacturing of synthetic detergent. LAB is usually mixture of C_9–C_{14} alkylbenzene obtained by the alkylation of benzene with mixed olefins using hydrofluoric acid or aluminum chloride as the catalysts. Owing to the hazardous nature of these catalysts, efforts have been made to develop environmentally benign catalysts, such as heteropolyacids (Sebulsky and Henke, 1971; Wen Langyou, 2000), H-ZSM-5, H-ZSM-12, HY (Cao et al., 1999), clays (Kocal, 1991), H-mordenite (Knifton and Anantanezi, 1998), and ionic liquid (Sherif et al., 1998). The Detal process, jointly developed by CEPSA and UOP, is a solid catalyst, fixed bed process which was commercialized in the 1990s, and has become the most modern technology for production of LAB.

In recent years, catalytic distillation (CD), a combination of distillation and reaction inside a single column, has become a hot issue in academic research and industrial practice (Zhu and Shen, 1995; Kumar and Daoutidis, 1999; Taylor & Krishna, 2000; Towler & Frey, 2000). Compared with traditional reactor-followed-by-distillation process, catalytic distillation has more remarkable advantages: significant capital savings, improved reaction conversion and selectivity, heat integration

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benefits, and so on (see Malone and Doherty, 2000). Catalytic distillation is suitable for alkylation reactions if given appropriate catalyst and recently Hunstman company has applied it to LAB synthesis (Knifton and Anantaneni, 1998).

Suspension catalytic distillation (SCD) has been developed recently for LAB synthesis by Research Institute of Petroleum Process, China, in which a new-developed supported heteropoly acid catalyst is adopted. In SCD process, the fine catalyst particles are suspended in the liquid within a tray column. Exploratory experiment of this new process in bench scale has already been carried out with promising results showing that it is an advanced technology for the production of LAB and is worthwhile for further R&D efforts. Recently, a pilot plant of SCD process with sieve tray column for cumene synthesis has been run for several months in Beijing Yanshan Petrochemical Co., Ltd. (BYPC), China.

As a part of the systematical study on suspension catalytic distillation for synthesis of LAB, in this work a rate-based model and simulator RaCOLUMN are developed and used for simulation of SCD process. Simulation results are discussed and compared with the experimental data.

SCD process for LAB synthesis

In order to develop environmentally benign process for LAB production, both a novel solid acid catalyst, the supported PW (12-tungstopphosphoric, $H_3PW_{12}O_{40} \cdot xH_2O$) heteropoly acid catalyst, and a new process, suspension catalytic distillation, have been investigated. It was found that, compared with HY and Hβ, PW heteropoly acid has much stronger acid sites, which effectively promote the alkylation reaction even under room temperature (20°C) and produce more desirable 2-phenyldodecane isomer. After supported on silica, both the specific activity and stability of PW heteropoly acid are considerably improved. Then, industrial olefins and benzene were used as the reactants to test the catalytic performance of PW/SiO_2. Unfortunately, it was found that the catalyst was deactivated quickly by industrial feedstock. The impurities, which deactivate the catalyst, are water, diolefins, and aromatics in the feedstock. The feedstock should contain less than 20 μg/g water, 0.05% diolefins, and 1% aromatics when PW/SiO_2 is used as the alkylation catalyst.

In order to further improve the performance of the PW/SiO_2 catalyst, a special silica carrier (H) has been selected from a number of silica. A series of catalysts of tungstophosphoric acid supported on SiO_2 with different textual properties were prepared by saturately impregnated method. The support of SiO_2 was impregnated with tungstophosphoric acid under continuous stirring at room-temperature. Then, it was filtered and dried at 120°C for 2–3 h. The catalyst was then calcined in air in a muffle furnace at 150–350°C for about 3 h. Typically, the textual properties of prepared catalysts were reported in the article (Zhang Jinchang et al., 2003a, b) and also are summarized in Table 1. Comparison of catalytic activity among different silica carrier supported HPW catalysts can be seen from Table 2. The last number of the catalyst mark is referred to as the different silica carrier. Fluorine and metal atom have also been introduced into the supported catalyst. Lewis acid sites were detected on the F containing supported PW (PW-F/H), which is believed to be the reason why PW-F/H has better catalytic performance. The catalytic life, deactivation and regeneration properties have been also studied. PW-F/H was the most stable one among many catalyst tested. It can be used more than 50 times batchwise in autoclave reactor or run 400 h in fixed-bed reactors with 100% conversion. The deactivation of the catalyst is mainly caused by carbonaceous deposit on active sites. The life period of the catalyst can be prolonged to more than 1,000 h with periodical benzene washing during the run.

Table 1. Textual Properties of Prepared Catalysts

Catalyst ID	Catalyst Mark	BET Surface Area (m2/g)	Pore Volume (ml/g)	Pore Diameter (nm)
1	PW/A	308	0.168	2.0
2	PW/B	279	0.176	3.1
3	PW/C	277	0.365	4.5
4	PW/D	264	0.424	5.0
5	PW/E	213	0.532	9.1
6	PW/F	200	0.542	9.0
7	PW/G	171	0.837	18.6
8	PW/H	111	0.928	32.1

A new process, SCD process, has been studied for the production of LAB. SCD process is a new kind of heterogeneously catalyzed reactive distillation in which the catalyst particles are suspended in the liquid and recirculated via a separator equipped without the column. Experimental setup of SCD for LAB synthesis with benzene and industrial olefins is given in Figure 1. A stainless steel tray column has 23 sieve trays and internal diameter of 50 mm was adopted. The operation pressure was set at 0.1, 0.13 and 0.16 MPa, respectively. The column was equipped with a total condenser on the top and distillate rates can be controlled by a reflux ratio adjustor. The column was supplied with protective heating to ensure adiabatic operation. There was a temperature-measuring probe or a sampling orifice on each sieve tray alternatively to measure temperature or analyze composition of liquid phase. The temperature, pressure and liquid level in the column were controlled and adjusted through a programmable logic controller (PLC) and a computer.

After being mixed well, the single liquid feed including benzene, industrial olefins and catalyst particles was fed to the tray 6 (counted from the top to the bottom). The catalyst separator was placed between the tray 15 and tray 16. The number of sieve trays in rectifying, reaction, and stripping section was 5, 10 and 8, respectively. The supported PW/F-H catalyst as mentioned earlier, was adopted in the experiment and had the concentration 50 g/L. The top reflux flow rate was 700 g/h. Other column parameters and sieve tray specification are given in Table 3. On the basis of exploratory experiments of LAB synthesis using PW/F-H catalyst, the SCD process can give the following promising results: 100% conversion of olefins, almost 100% selectivity and high quality LAB product with more 2-LAB isomer, and less tetralins impurities, under very mild conditions of 0.05 MPa (gauge), low temperature (90–100°C) and low benzene/olefin mole ratio (1).

At present, in traditional CD column catalyst pellets are most commonly enveloped within wire gauze envelopes and then packed inside the column. Although these envelopes could minimize the potential of losing the catalyst pellets in case the packing were damaged, it will substantially reduce the effectiveness of catalyst due to limiting the mass and heat transfer

Table 2. The Comparison of Catalytic Activity for Different Silica Carrier Supported HPW

Catalyst	PW/A	PW/B	PW/C	PW/D	PW/E	PW/F	PW/G	PW/H
[a]Laboratory reagent, %	14.3	12.6	90.5	65.7	95.3	87.5	100	61.5
[b]Industrial stock, %	45.6	48.3	56.5	42.7	68.3	70.5	75.4	100

Note: (a) 80°C, 25 ml benzene (analytical) + 5 ml dodecene (chemical) + 0.25 g catalyst, reaction time 15 min.
(b) 95°C, 25 ml benzene (industrial) + 25 ml industrial olefins (refined) + 2.5 g catalyst, reaction time 30 min.

between the catalyst pellets and the fluid around them. In addition, catalyst regeneration and prefabrication of catalyst envelops in this configuration are very inconvenient. SCD process has the same advantages as the conventional catalytic distillation, and the flowing catalyst particles can be conveniently removed and regenerated online. In addition, the catalytic efficiency is remarkably improved and the amount of catalyst used in the reactive section is, therefore, reduced. In summary, the primary studies indicate that SCD process with PW/SiO_2 catalyst is an advanced technology for LAB manufacture, and it is worthwhile for further R&D efforts.

In the earlier development practice of the SCD process, researchers were afraid of solids accumulation problems on the sieve trays. The effect of catalyst granularity on the process was first studied by using silica gel particles with different diameters, and found that the appropriate range of catalyst diameter is 10–50 μm. During the three-month experiment in the lab column, the SCD process ran well, and accumulation of catalyst particles was not found. In addition, a pilot plant of SCD process for cumene synthesis has been run for several months in BYPC, and the results were also good with not finding the solids accumulation phenomenon. In fact, two filters alternatively operated are placed before the product separation system to avoid a very small amount of the catalyst to be carried into the separation unit. However, there are also several considerable problems when applying SCD to industrial practical. Adding a solid/liquid separator between the reactive and stripping sections makes it a more complicated system to design and control, especially with recycled catalyst suspension playing an important role in the SCD column. In addition, potential solids accumulation problems on commercial sieve trays, and catalyst abrasion and effect of catalyst particles on mass and heat transfer at the vapor-liquid interface should be considered.

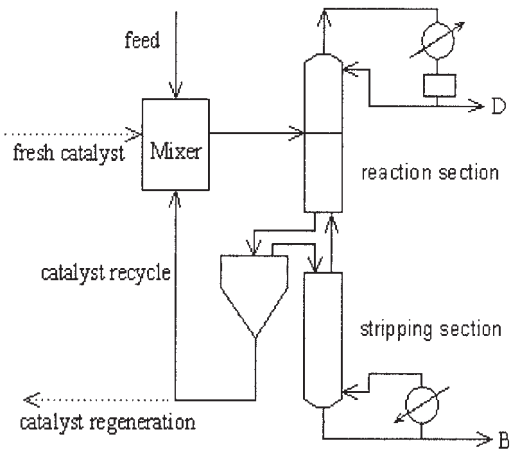

Figure 1. Suspension catalytic distillation.

Rate-based modeling and simulator RaCOLUMN

There are mainly two distinctly different approaches in the literature to simulate traditional distillation and catalytic distillation: the equilibrium stage model (Nelson, 1971; Venkataraman et al., 1990; Pilavachi et al., 1997), and the rate-based model (Pinjala et al., 1992; Lee and Dudukovic, 1998; Higler et al., 1998, 1999a, b; Baur et al., 1999). In the case of catalytic distillation, the chemical reaction has to be additionally taken into account, either via reaction equilibrium equations, or via rate expressions integrated into the mass and energy balances. The equilibrium stage (EQ) model assumes that the vapor stream leaving a tray or a packing segment is in thermodynamic equilibrium with the correspondent liquid stream leaving the same tray or segment, but such an approach can hardly give a required modeling accuracy, since reactive distillation is determined by kinetically controlled steps like mass transfer or reactions. In a rate-based approach actual rates of mass transport, heat transport and chemical reactions are directly taken into account, so it is a more physically consistent, and generally can give better simulation results compared with the EQ model. However, a great amount of design information must be specified for the rate-based model to calculate mass-transfer coefficient, interfacial area and liquid holdups. In addition, more physical properties such as surface tension, diffusion coefficients, viscosities, for example, are required.

Being a new process, SCD has hardly been modeled in the open literatures. In this work, the rate-based approach is adopted to develop a simulator used in SCD process, RaCOLUMN, and as a case study using the simulator the SCD process is explored for LAB synthesis. A representation of the rate-based model at a specified position in a tray or packed column is shown in Figure 2, which rests on the following simplifying assumptions:

Table 3. SCD Column Specifications for LAB Synthesis

Type of tray	Sieve
Column diameter (m)	0.05
Total tray area (m^2)	1.963×10^{-3}
Number of liquid flow passes	1
Tray spacing (m)	0.1
Liquid flow path length (m)	0.045
Active area (m^2)	1.586×10^{-3}
Total hole area (m^2)	1.74×10^{-4}
Weir length (m)	0.015
Weir height (m)	0.01
Weir type	segmental
Downcomer clearance (m)	0.008
Deck thickness (m)	0.002

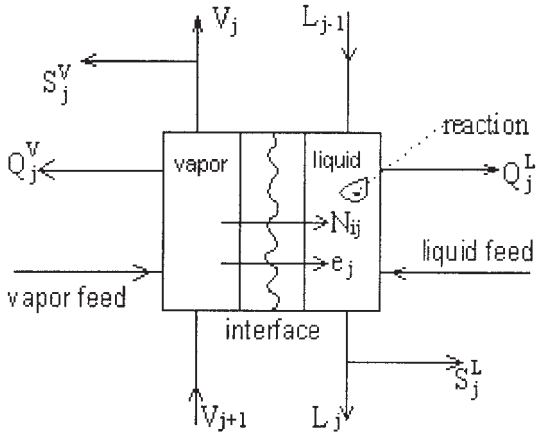

Figure 2. Rate-based model for SCD column.

- steady-state conditions;
- one-dimensional (1-D) flow of vapor and liquid phases;
- dispersion at uniform pressure with adiabatic boundaries;
- reactions take place only in liquid phase;
- no resistance to mass transfer at the interface, local phase equilibrium;
- no mass and energy accumulation at the interface.

In addition, for a heterogeneous reaction, there are two basic ways to describe the reaction term: one is to simply treat the reaction pseudohomogeneously, and another needs detailed description of diffusion and reaction inside the catalyst particles. However, in the SCD process the catalyst particles are perfectly dispersed in the liquid phase and they are so small (10–100 μm) that the reactions can be considered to be pseudohomogenous. It should be noted that the simulator, RaCOLUMN, developed in this work does not include modeling the pore diffusion, but rather the macrokinetics obtained under reaction conditions similar to the SCD experimental investigation, is used in the model. It means that the pore diffusion resistances are included in the macrokinetic equations. Modeling pore diffusion is very complicated, especially for multicomponent liquid diffusion. Although a dusty fluid model was developed by Krishna and Wesselingh (1997), there are no reliable methods for evaluating nonideal thermodynamic behavior inside a catalyst particle (Higler et al., 2000).

In the SCD process, an additional important problem is the simulation of the solid/liquid separator, which is also the difference from traditional CD processes. In general, almost all of the catalysts are sedimentated, and the catalysts in the stripping section and the reboiler of the SCD column were not yet found in experimental investigation. For steady-state simulation, the liquid in the recycled catalyst suspension can be treated simply as a liquid sidestream between the reaction section and the stripping sections. In fact, the amount of the liquid in recycled catalyst suspension has important effect on dynamic characteristic of the SCD process and column performance. This effect will be discussed in another article.

On the basis of the earlier assumptions, we can write the mass and energy balance equations separately for vapor and liquid phases as done in many literatures. It is established that transfers from the vapor phase to the liquid phase is positive. The terms relevant to chemical reactions are only included in the liquid-phase balance equations

$$0 = L_j + S_j^L - L_{j-1} - F_j^L - \sum_{k=1}^{m}\sum_{i=1}^{n} \nu_{ik} r_{jk} \varepsilon_j - N_{Tj} \quad (1)$$

$$0 = (L_j + S_j^L)\, x_{ij} - L_{j-1} x_{ij-1} - F_j^L x_{ij}^F - \sum_{k=1}^{m} \nu_{ik} r_{jk} \varepsilon_j - N_{ij}^L, \quad i = 1, \cdots, n \quad (2)$$

where N_{ij} is the interface transfer rate, and r_{jk} is the rate of reaction k on the stage j. ν_{ik} represents the stoichiometric coefficient of the component i in the reaction k, and ε_j represents the reaction volume.

At the vapor-liquid interface, the thermodynamic equilibrium between the two phases is assumed

$$y_{ij}^I = K_{ij} x_{ij}^I, \quad i = 1, \cdots, n \quad (3)$$

The summation equations for the mole fractions are also needed in each phase and the interface

$$\sum_{i=1}^{n} y_{ij} - 1 = 0, \quad \sum_{i=1}^{n} x_{ij} - 1 = 0, \quad (4)$$

$$\sum_{i=1}^{n} y_{ij}^I - 1 = 0, \quad \sum_{i=1}^{n} x_{ij}^I - 1 = 0, \quad (5)$$

Mass transfer through interface is modeled as a combination of the two-film model presentation (Lewis and Whitman, 1924), and rigorous Maxwell-Stefan diffusion description (Hirschfelder et al., 1964), and written in terms of transfer coefficients as follows (Taylor and Krishna, 1993)

$$(N^V) = C_t^V a^I [R_V]^{-1} (y^V - y^I) + (y^V) N_T \quad (6)$$

$$(N^L) = C_t^L a^I [R_L]^{-1} (x^I - x^L) + (x^L) N_T \quad (7)$$

$$E^V = h_V a^I (T^V - T^I) + \sum_{i=1}^{n} N_i^V \bar{H}_i^V \quad (8)$$

$$E^L = h_L a^I (T^I - T^L) + \sum_{i=1}^{n} N_i^L \bar{H}_i^L \quad (9)$$

The mass-transfer model is the most important part of the rate-based distillation model, and the behavior of a distillation column will be changed if selecting different mass-transfer correlations for estimating mass-transfer coefficient. Many kinds of mass-transfer models per internals type are available from open literatures and already incorporated in RaCOLUMN.

The reboiler and condenser of SCD column are modeled as equilibrium stages.

Although it is developed for SCD process simulation,

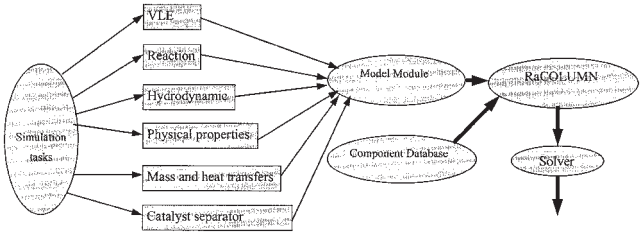

Figure 3. Structure of RaCOLUMN.

RaCOLUMN is also a completely rate-based simulator for traditional distillation or catalytic distillation. Several important parts of the RaCOLUMN are presented in Figure 3, and it will automatically call on different parts to accomplish the specified simulation tasks. The solver uses Newton's method, and different variants of the equilibrium stage model can be used for the initialization.

Simulation Results and Discussion

The experimental data for LAB synthesis in a bench-scale SCD column are used to test RaCOLUMN reliability and accuracy. Experimental setup of SCD has already been presented in the previous section of SCD process for LAB synthesis.

Industrial olefins in the feedstock were mainly hydrocarbon mixtures as shown in Table 4, and it is difficult to simulate for so many components. First, for simplification, the whole reaction system has to be lumped into a four-component one to make it easier to simulate, and then a more complex seven-component system is adopted. In the four-component system, *n*-dodecane is used to stand for the paraffin hydrocarbons (C_{10}–C_{13}) and 1-dodecene for the olefin hydrocarbons (C_{10}–C_{13}) in straight chain form due to their similar properties. In the seven-component system three more components, *n*-decane, *n*-undecane and *n*-tridecane, are added. Finally, simplified feed composition is shown in Table 5.

The alkylation reaction of LAB synthesis can be expressed as

$$C_6H_6 + C_{12}H_{24} \Leftrightarrow LAB, \quad \Delta H^{\Theta}_{298} = -24.7 \text{ KJ/mol}$$

Table 4. Composition of Industrial Olefins

Constitution		wt/%
Straight chain hydrocarbons		96
Non straight chain hydrocarbons		2.6
Aromatic hydrocarbons		1.2
Diolefins		0.04
Water		0.002
Unknown		0.18
Total		100
Distribution of Straight Chain Hydrocarbons	Paraffin Hydrocarbons	Olefin Hydrocarbons
$\leq C_9$	0.2	
C_{10}	16.7	1.4
C_{11}	32.2	3.2
C_{12}	24.9	3.0
C_{13}	12.3	2.1
Total	86.3	9.7

Table 5. Simplified Composition in Feed

	Four Component System	Seven Component System
Number of components	4	7
Feed temperature (K)	388	388
Feed pressure (MPa)	0.1	0.1
Feed component flow rate (mol/h)		
Benzene	0.448	0.448
1-dodecene	0.41	0.41
LAB	0.	0.
n-dodecane	4.2	1.169
n-decane		0.939
n-undecane		1.648
n-tridecane		0.5357

which is moderately exothermic and can be seen as irreversible reaction owing to large value of reaction equilibrium constant. In addition, there are other undesirable side reactions in this system, such as further alkylation reactions of LAB with olefin and dimerization of olefins.

The reaction rate equation for LAB synthesis has been little cited in literatures, in particular with the supported PW heteropoly acid as catalyst. Reaction rate data were measured using benzene and 1-dodecene as reactants. However, dodecane is also added into the reaction system to approximate the composition of industry raw material, and the mole fraction of these three materials (benzene, dodecane, dodecene) is 0.645, 0.32 and 0.035, respectively. Alkylation reactions usually take place under high ratio of benzene to olefins, so reaction rate data were treated in pseudo first-order form, and afterwards implemented directly into the RaCOLUMN code as follows

$$-\frac{dC_{12}}{dt} = k_s C_{12}$$

$$k_s = 4.89 \times 10^4 \exp(-36000/RT) \text{ min}^{-1}$$

where C_{12} represents for concentration of 1-dodecene in the liquid phase. From the simulation result in Figure 6a, the ratio of benzene to 1-dodecene is very high, which also proves this assumption.

The UNIFAC model is adopted for describing of nonideality of the liquid phase, while the Soave-Redlich-Kwong equation of state is used for the vapor phase. The Antoine equation is used for calculating of the vapor pressure. Thermodynamic data are taken from Reid et al. (1987). In addition, the isobaric ideal gas heat capacity of LAB is estimated by using Rihani-Doraiswamy method (Lu Huanzhang et al., 1994). The liquid-phase binary diffusivities are determined using the method of Wilke-Change (see Reid et al., 1987) for the diluted mixtures, and then corrected by the Vignes equation (Taylor and Krishna, 1993), and the Fuller-Schettler-Giddings method for vapor-phase binary diffusivities. Mass-transfer coefficients are calculated from the correlations of Chan-Fair (1984), and Zuiderweg (1982) correlations for interface area. Different Zuiderweg correlations should be used in the spray regime form or the froth emulsion regime, respectively, and they are valid for the Fractionation Research Inc. (FRI) experiments for which they were derived. For general application, information is required on the effect of hardware variations and of system variations.

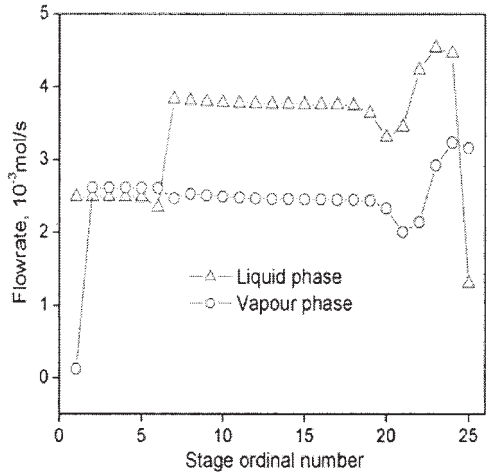

Figure 4. Liquid and vapor phase flow rates.

The interface area will vary a little with temperature and composition from tray-to-tray.

Figures 4–10 display the simulation results by RaCOLUMN simulator. In these figures, the ordinal number of each tray is counted from the column top to the bottom with the ordinal number 1 for the condenser, and 25 for the reboiler. In Figure 4 the liquid and vapor molar flow rates are shown. The increase in the step-way in the liquid flow rate from tray 6 to tray 7 is due to the liquid phase feed at tray 7. The vapor flow rate is nearly constant throughout the column. However, near the bottom, there are obvious changes in both flow rates. This may be caused by large mass-transfer rates through the vapor/liquid interface, which can also be seen in the following Figure 7.

The experimental and simulated profiles of liquid temperature along the column are shown in Figure 5. It is obvious that the temperature profile of the seven-component system is closer to the experimental values than that of the four-component system. From Figure 5, we can see that the liquid temperature in the upper part of the SCD column changes only slightly, while increases rapidly in the stripping section espe-

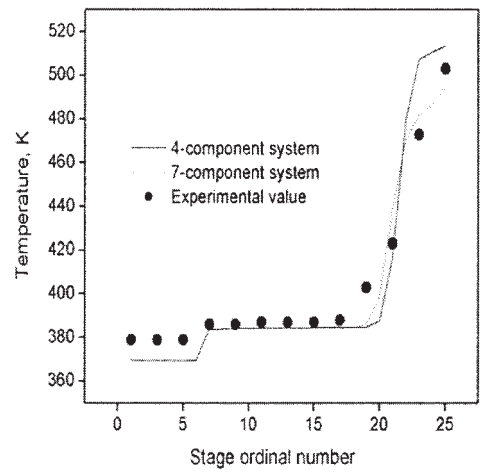

Figure 5. Comparison of liquid temperature profiles predicted (by the model) with experimental data at 0.16 MPa.

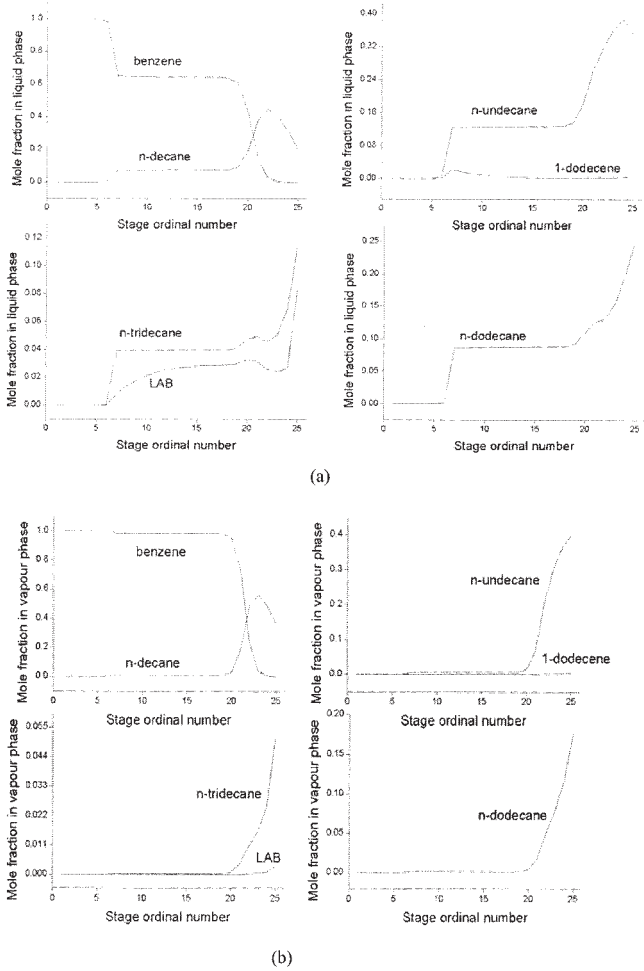

Figure 6. Composition profiles of liquid and vapor phases predicted by the seven-component model: (a) liquid; (b) vapor.

cially near the bottom of the column, which is corresponding to different local compositions as pointed out in Figure 6. At the top of the SCD column vapor of pure benzene is introduced into the condenser and the condensate refluxes to the column, in addition, no reaction takes place, so the liquid temperature in the rectifying section is almost equal to the boiling point at corresponding pressure. In the reactive section, the concentration of benzene decreases and other heavier components appear owing to feed and alkylation of benzene, resulting in temperature increase compared with the rectifying section. In this section, benzene still maintains a high concentration and its value changes a little, so the liquid temperature nearly maintains invariably. In the stages near the bottom, most of the benzene is stripped and goes back to the reaction section so that its concentration decreases rapidly while the amount of other heavier components increases, leading to a substantial increase of temperature. From earlier, we can see that the trays near the bottom can be used as sensitive plates to control the operating temperature of the SCD column.

Figure 6 displays the composition profiles in the bulk liquid and bulk vapor phases. For a given set of operating conditions listed in Table 5, the RaCOLUMN predicts that the concentration of LAB in the bottom stream is about 8.33% (mol). In

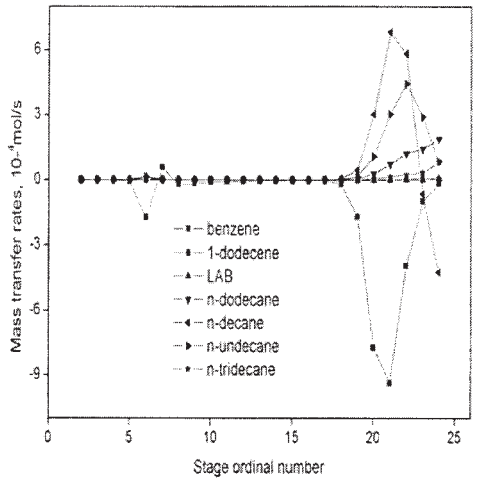

Figure 7. Profiles of interphase mass-transfer rates of different components.

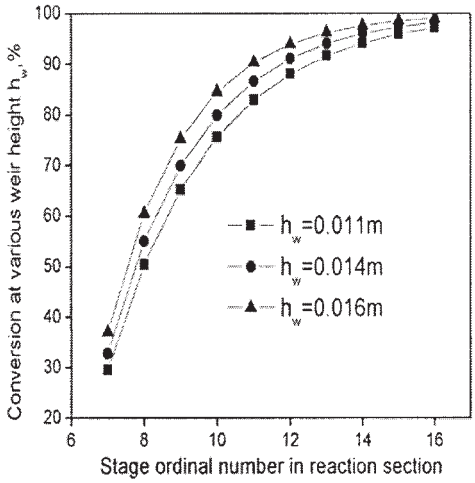

Figure 9. Conversion profiles of l-dodecene at various weir height h_w.

addition, we can see that benzene maintains a high concentration in the reactive section. This not only prolongs the life of the catalyst owing to washing catalyst particles continuously, but also increases the ratio of benzene to olefin in the reactive section, thus, may inhibit the polymerization of olefins and other side-reactions.

The profiles of the mass-transfer rates of the different components in every stage along the column, N_{ij}, are shown in Figure 7. It can be seen that the interphase mass-transfer rates of almost all components are equal to zero in the rectifying and reactive sections of the SCD column, so interface mass transfer hardly takes place there. However, on the several trays near the bottom the mass transfer rates differ greatly of which benzene has a large negative value, while other heavy components have positive values. This means that benzene is stripping to the vapor phase near the bottom, and other heavy components is transferring in the opposite direction. Correspondingly, the concentration of benzene in the liquid phase decreases quickly and other components increase, which can also be seen from Figure 6. Since the main transfer of mass takes place on the trays near the bottom, the stripping section should be designed specially to improve mass transfer between liquid and vapor phases.

The comparison of simulated conversion of 1-dodecene with the experimental data is shown in Figure 8. The liquid composition is analyzed on every other tray by a GC of GC8000 (Carlo Erba (CE) company, Italy). The conversion is calculated based on the 1-dodecene concentration. Obviously, the model prediction satisfactorily agrees with the experimental observation. In order to probe the influence of tray design on conversion, simulation computations were accomplished for different weir heights, and the results are displayed in Figure 9. It is seen that increasing the weir height leads to improved conversion of 1-dodecene, because the clear liquid height and the corresponding residence time of the liquid phase increase, and this is favorable for reaction.

The influence of operation pressure on the temperature profile of the liquid phase in the SCD column can be seen from Figure 10. With raising operation pressure, the temperature of the liquid phase will increase, correspondingly. Through regulating the operating pressure, distillation, and reaction temperatures can be controlled and adjusted to match suitable

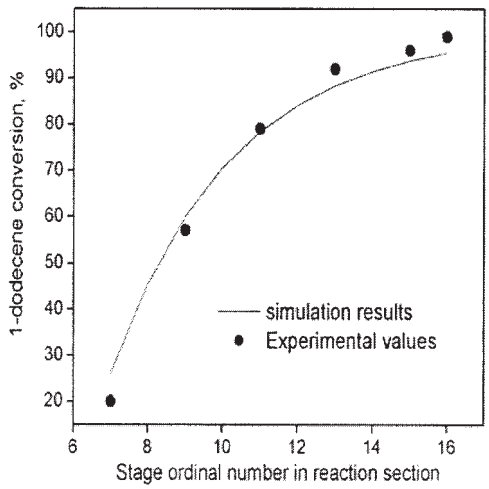

Figure 8. Conversion profile of l-dodecene at 0.16 MPa.

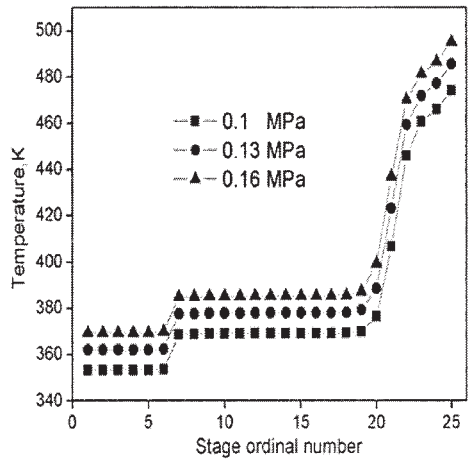

Figure 10. Simulated temperature profiles in liquid-phase at different pressures.

reaction temperature of the catalyst. In the case studied here, activation temperature of catalyst is about 360–380 K.

When a chemical reaction takes place in a distillation column, there is always an associated release or consumption of heat. If the reaction is exothermic, the heat of reaction can be used to provide the heat of vaporization and reduce the reboiler duty. RaCOLUMN can automatically calculate the heat of reaction and provide information on heat integration in the case of catalytic distillation. As for LAB synthesis by SCD, RaCOLUMN predicts that ratio of reaction heat to reboiler duty is about 8%, which indicates considerable energy saving.

Conclusions

Suspension catalytic distillation with supported PW heteropoly acid catalyst, as a new environmentally benign process for synthesis of LAB, has shown many advantages compared with a traditional process. However, the adding of solid/liquid catalyst separator makes it more difficult for simulation, design and control. A rate-based simulator (RaCOLUMN) was developed, and the characteristics of SCD process were studied by means of this simulator. The simulation temperature and 1-dodecene conversion profiles along the SCD column are in good agreement with the experimental data obtained in a bench scale SCD column. Simulation results show that separation of the mixture takes place in the stripping section, mainly, and the distillation effect leads to the high ratio of benzene to olefin in the reactive section, even though this ratio in the feed is almost near to 1:1. This obviously is favorable for inhibiting polymerization of olefins and other side-reactions.

The rate-based simulator RaCOLUMN is quite general and could also be used for the design and simulation of different SCD processes.

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Notation

a = area, m^2
c = number of components
C_t = total concentration, mol/m^3
E = energy transfer rate, J/s
F = feedstream, mol/s
h_w = weir height, m
H = molar enthalpy, J/mol
h = heat-transfer coefficient, $W/m^2 \cdot K$
k_s = reaction rate constant, min^{-1}
K = vapour-liquid equilibrium constant
L = liquid flow rate, mol/s
N = mass-transfer rate, mol/s
Q = heat duty, J/s
r = reaction rate, $mol/m^3 \cdot s$
R = gas constant, $J/mol \cdot K$
R_L = rate matrix for liquid phase
R_V = rate matrix for vapor phase
S = sidestream flow rate, mol/s
T = temperature, K
V = vapor flow rate, mol/s
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek letters

ε = reaction volume, m^3
ν = stoichiometric coefficient

Subscripts

i = component index
j = stage index
k = alternative component index
m = reaction index
t = total

Superscripts

F = referring to feed stream
I = referring to interface
L = referring to liquid phase
V = referring to vapor phase

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