# PROCESS ESTERIFICATION AND PRODUCT QUALITY SIMULATION

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## Abstract

A process model for esters production was developed and corresponding parameters were determined. The synthetic esters production with apple and lemon smelts: ethyl-acetate and three-ethyl-citrate are simulated. The system approach which permits the evaluation of feasibility and operations integration, always for predicted behavior of the process was used. Generic data of kinetic parameters was developed as a relational data base which linked kinetic models and operation simulation. The integration procedure was generated and ranked data base kinetic parameters and kinetic models which define product quality changes. Reaction operation with distillation operation were simulated with derived mathematical models. The product quality object function was examined to find the best feed of reactants. Simulation was carried out for various operation regions, conditions and product quality. Operation makes history data of manipulates and object variables, and performs dynamic simulation. Steady state and unsteady state process behaviors were simulated. The startup and product process period were examined. The operation of the process esterification was analyzed to identify optimum conditions. The obtained simulated results have shown high quality of the product and with in a good agreement with experimental data.

**Keywords: Simulation model, Analyzer, Product quality simulation, Advanced numerical methods.**

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## 1 Introduction

A new approach in the computerized modeling is represented directly by the structure of the elementary transitions referring to the various phenomenological define chemical reactions.

The knowledge based system which automated the process, enabling engineers to perform modeling and simulation study was investigated. Input data linked with routines for kinetic parameters determination.

Kinetic models of the ethyl esters formation was derived and energy activation and frequency factor were determined. The specific chemical rate constant was determined and analysis of the product dynamic was performed.

As a case study the esterification with distillation was used. The synthetic esters production with apple and lemon smelts: ethyl-acetate and three-ethyl-citrate are simulated.

## 2 The examined process

Compared to the processes in regular distillation, the processes in reaction distillation are extremely complex. The combination of a reversible reaction in the liquid phase and distillation is a widely used technique to enhance the conversion of reactants to levels above those of equilibrium conversion. The choice of optimum equipment for such a combined process is influenced by reaction rate and by the required separation efficiency. The combination of a reversible liquid phase reaction with distillation in a reaction column often leads to increased conversion but also has disadvantages which are particulary manifest when the reaction is catalysed by a mineral acid. In such a case the product must be separated from the acid by vaporization, and product losses do occur. An alternative to homogenous catalysis with mineral acid is provided by heterogenous catalysis.

In this paper the effects of separation and esterification rate were simulated. The mathematical models were developed by introducing reaction functions in material and enthalpy balance equations for startup and product periods. An algorithm and programme's routines were developed to simulate the effect of separation, esterification rate and yields.

## 3 Kinetics models of esters formation
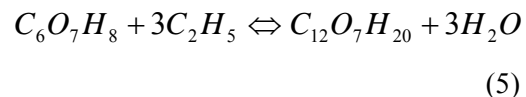
Reaction esterification in the liquid phase:

$$aA + bB \Leftrightarrow cC + dD \qquad (1)$$

for ethyl-acetate formation,

$$CH_3COOH + C_2H_5OH \Leftrightarrow CH_3COOC_2H_5 + H_2O \quad (2)$$
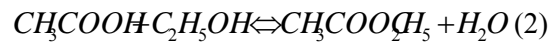
$$\frac{dc_A}{dt} = \frac{dc_B}{dt} = -(k_1 c_A c_B - k_1' c_A c_B) \qquad (3)$$

$$\frac{dc_c}{dt} = \frac{dc_D}{dt} = k_1 c_A c_B - k_1' c_C c_D \qquad (4)$$

and for the three- ethyl- citrate ,

$$C_6 O_7 H_8 + 3C_2 H_5 \Leftrightarrow C_{12} O_7 H_{20} + 3H_2 O$$

$$(5)$$

$$\frac{dc_A}{dt} = \frac{1}{3}[-(k_2 c_A c_B - k_2' c_A c_B)] \qquad (6)$$

$$\frac{dc_B}{dt} = -(k_2 c_A c_B - k_2' c_A c_B) \qquad (7)$$

$$\frac{dc_C}{dt} = \frac{1}{3}(k_2 c_A c_B - k_2' c_A c_B) \qquad (8)$$

$$\frac{dc_D}{dt} = (k_2 c_A c_B - k_2' c_A c_B) \qquad (9)$$

For these reactions, reaction rate is formulated as following:

$$v = A_0 e^{-E/RT} c_A^{n_A} c_B^{n_B}$$

and reaction order $n = n_A + n_B$.

## 4 Process model building

The structure of  different modules for simulation  is shown in Fig.1.

START

INPUT DATA

Mathematical models

Numerical algorithms

*Matlab* package

*Dinrp* package
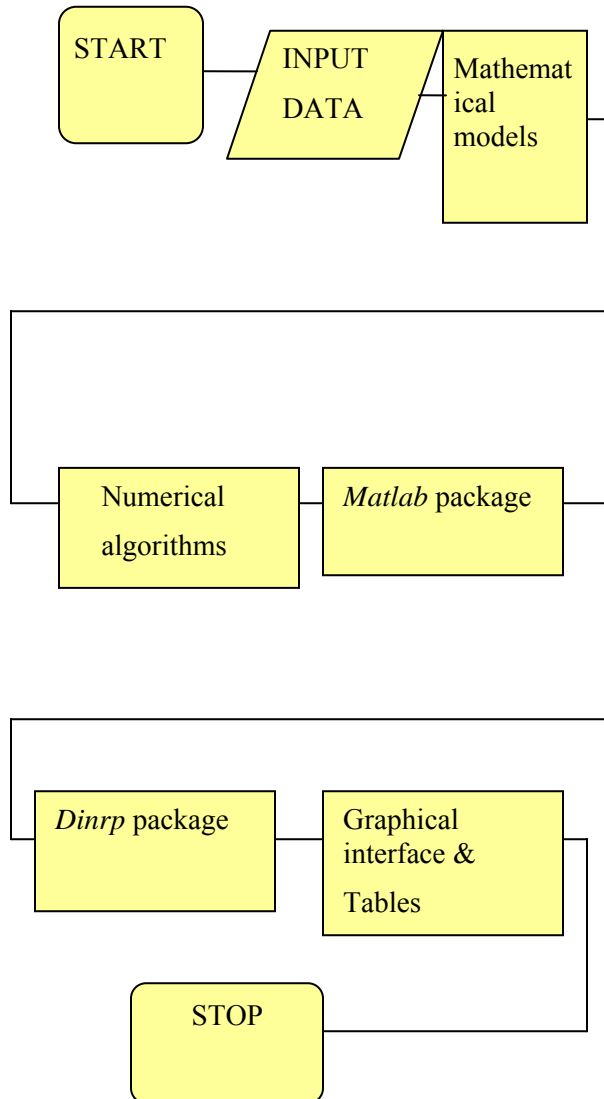
Graphical interface & Tables

STOP

Fig1. Simulation model

The synthesizing procedure is generated and ranked database facts and clauses, kinetic parameters and kinetic models which defined product concentration changes.

The corresponding software development was performed in the Matlab and Dinrp program packages environment.

The chemical kinetic parameters were determined by Optimap software package. The obtained values of energy activation,

acceleration factor and specific chemical reaction rate constant  for three-ethyl-citrate are given in Table 1.

The obtained values of energy activation and acceleration factor for ethyl-acetate are given in Table 2.

## 5 Product quality simulation

The synthetic esters production with apple and citric smelts, ethyl-acetate and three – ethyl-citrate, respectively are simulated.

For three  ethyl-citrate simulation was carried out for reactants ratio from 1:3 to 1:6. The simulated results have been in a good agreement with previous experimental one. The obtained results show better yields for ester with one mole of citric acid and six moles of ethanol.

Fig.2 shows concentration changes of three ethyl-citrate vs. time for initial reactants ratio 1:3.

Fig. 3 shows product quality changes of ethyl- acetate production vs. time.
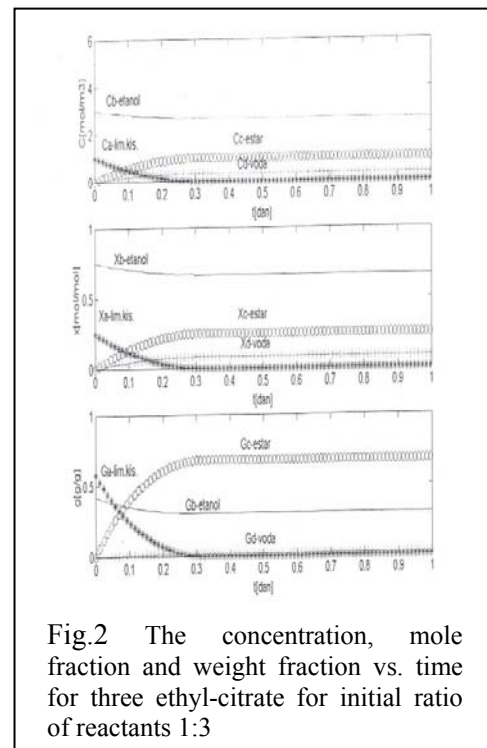
In Fg.4 three-ethyl-citrate quality has shown



Fig.2 The concentration, mole fraction and weight fraction vs. time for three ethyl-citrate for initial ratio of reactants 1:3

Fig.3 The product composition vs. time for ethyl-acetate for start up-period for reactants ratio 1:2



Fig.4 The product quality in mole fraction and weight fraction vs. time in day for three-ethyl-citrate for initial ratio of the reactants 1:6
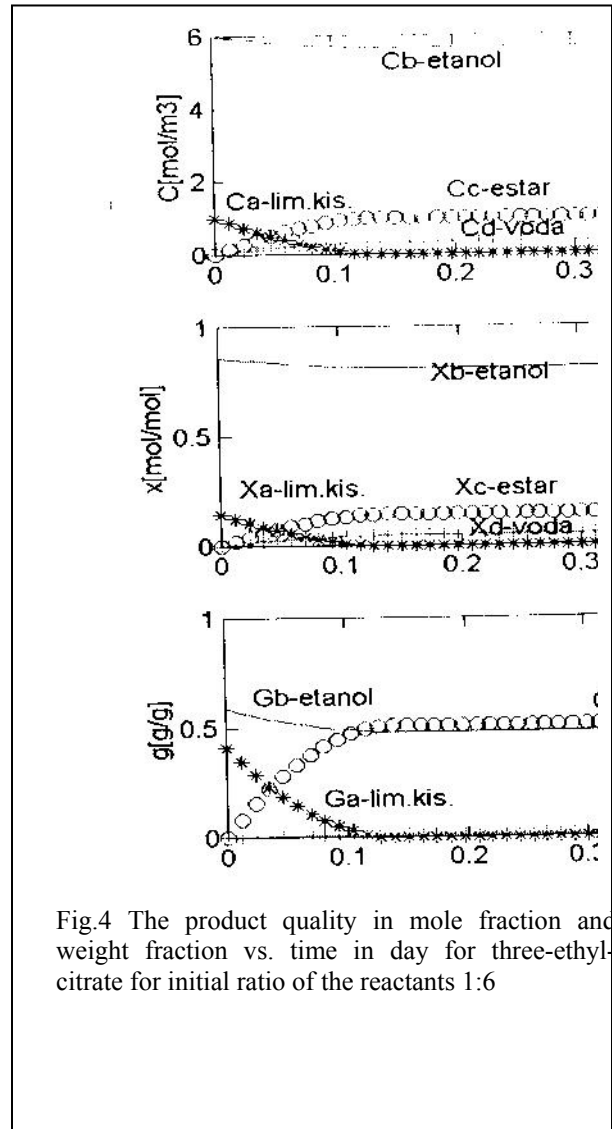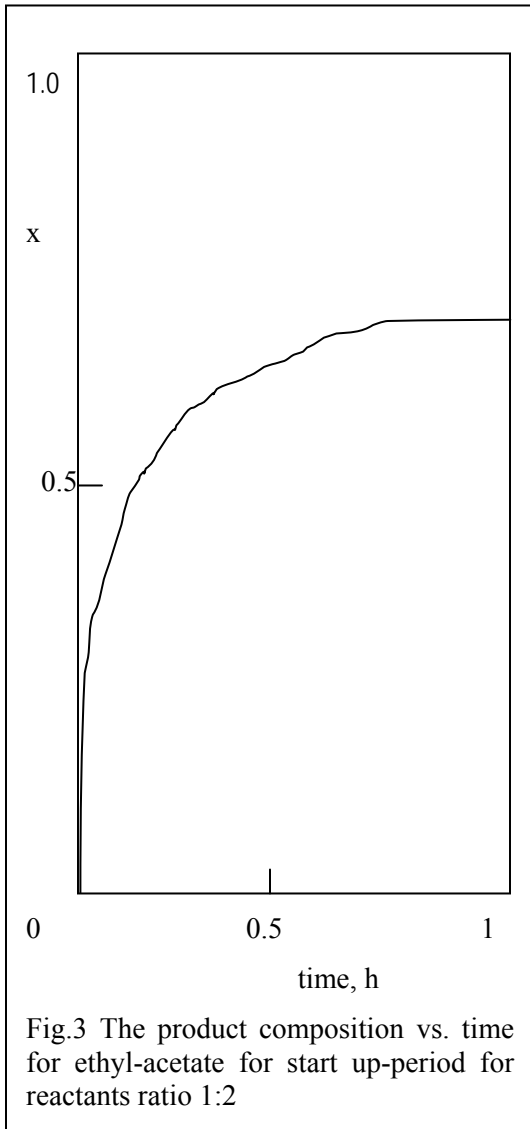
for initial reactants ratio 1:6. Fig.5 shows dynamic changes in start-up period for thee-ethyl- citrate.

The simulation results have shown fast dynamic changes in the first two hours. After two hours process goes slow in steady state conditions. Slow dynamic changes were

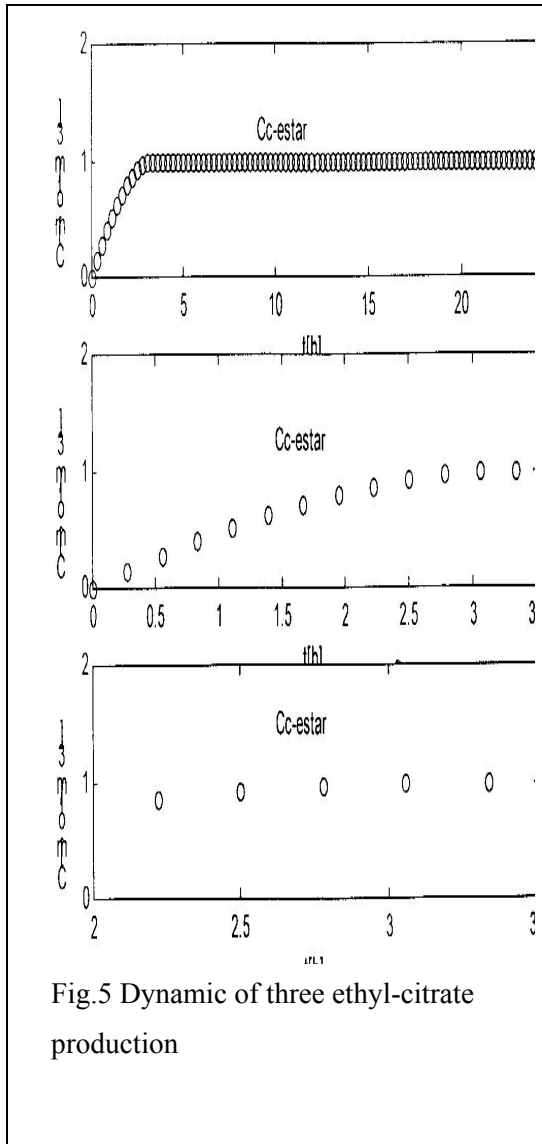obtained between 2 hours and 3.5 hours. After four hours process goes steady-state.

Fig.5 Dynamic of three ethyl-citrate production

Table 1. Parameters of kinetic model for ethyl-acetate

|  | $k_1, dm^3$ $mole^{-1} s^{-1}$ | E, J/mole | $A_0, dm^3$ $mole^{-1}$ $s^{-1}$ |
|---|---|---|---|
| Direct reaction | $k_1 = Ae^{-E/RT}$ | 17460 | 58.7 $10^{-3}$ |
| Reversible reaction | $k_1' = Ae^{-E/RT}$ | 16530 | 22.1 $10^{-3}$ |
| Reaction order | n=2 |  |  |

Table 2. Parameters of kinetic model for three-ethyl-citrate

|  | $k_1, m^3$ $mole^{-1} s^{-1}$ | E, J/mole | $A_0,$ $m^3 mole^{-1}$ $s^{-1}$ |
|---|---|---|---|
| Direct reaction | $8.84\ 10^{-6}$ | 147410.69 | $1.33\ 10^{-16}$ |
| Reversible reaction | $8.164$ $10^{-6}$ | 4907.433 | $4.49\ 10^{-5}$ |
| Reaction order | n=2 |  |  |

## 6 Conclusions

The synthetic esters production with apple and citric smelts, ethyl-acetate and three - ethyl-citrate are simulated. The product quality was examined to find the best feed of reactants.

Corresponding kinetic parameters were determined from previous experimental data base.

The process esterification was examined to identify optimal operation conditions.

The investigation results have shown high quality of the product and with in a good agreement with experimental data. The obtained results in this paper can be applied for the others esters production.

*Notation*

A-acid

B-ethanol

C-ester

D-water

$A_0$- acceleration factor, $m^3 mole^{-1\ s\ -1}$

C-concentration, $m^3/mole$

E-energy activation, J/mole

k- specific rate constants, m3 $mole^{-1} s^{-1}$

N-reaction order

X-mole fraction

*Subscript*

    A- acid

    B- ethanol

    C- ester

    D- water

    1-ethyl-acetate

    2-three-ethyl-acetate

*Superscript*

n-reaction order

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