**Journal of Petroleum Research and Studies**

**Open Access**
**Vol. 15, No. 2, June 2025, pp. 106-125**

**P- ISSN: 2220-5381**
**E- ISSN: 2710-1096**

DOI: http://doi.org/10.52716/jprs.v15i2.976

# Simulation Study of Methyl Salicylate Production via Reactive Distillation Columns

**Mohammed Jassim[1], Dhia Y. Aqar[2], Safaa M. R. Ahmed[1*]**

[1]Chemical Engineering Department, College of Engineering, Tikrit University, Tikrit, Iraq.

[2]Studies, Planning, and Follow up Directorate, Ministry of Oil, Baghdad, Iraq.

[*]Corresponding Author: Email: Safaamohamed@tu.edu.iq

Received 09/06/2024, Revised 05/08/2024, Accepted 08/08/2024, Published 22/06/2025



## Abstract

In this research, reactive distillation column simulation of methyl salicylate (MeSC) synthesis is well explored and discussed. Methyl salicylate is one of the common esters used in industries such as the manufacture of pharmaceuticals, fragrances and flavors and is produced through esterification of salicylic acid (ScA) and methanol (MeOH). Reactive distillation, which combines the reaction kinetics and separation operations together in the same vessel, can be regarded as a very effective approach. By Applying different parameters using the process simulation software, the best operating conditions for the formation of methyl salicylate were determined including the temperature and the types of columns. Here research is carried out with an aim of assessing the performances of batch (CBD) and semi batch (SBD) processes of reactive distillation and establish the conversion rates as well as the conversion efficiencies. The accomplishment of the production process simulation is facilitated by gPROMS Module Builder that can model more than simple reactions to produce high purity methyl salicylate through distillation. The paper also compares the efficiency of the SBD composition with the CBD methods, and the statistics differ significantly; the SBD composition has a 85% conversion rate and has the highest purity of 99%.

Insights from simulation provide valuable guidance for optimizing process parameters and selecting the most appropriate distillation mode for industrial-scale production. This research contributes to ongoing efforts to intensify the process and emphasizes the potential of reactive distillation as aviable method for methyl salicylate synthesis.

***Keywords:*** gPROMs, Methyl salicylate, Optimization, Reactive distillation, Simulation.

**Journal of Petroleum Research and Studies**

**Open Access**
**Vol. 15, No. 2, June 2025, pp. 106-125**

**P- ISSN: 2220-5381**
**E- ISSN: 2710-1096**

**دراسة محاكاة لإنتاج ميثيل ساليسيلات عبر أعمدة التقطير التفاعلية**

**الخلاصة:**

في هذا البحث، تم استكشاف ومناقشة محاكاة عمود التقطير التفاعلي لتصنيع ميثيل الساليسيلات .ميثيل الساليسيلات هو أحد الاسترات الشائعة المستخدمة في صناعات مثل صناعة الأدوية والعطور والنكهات ويتم إنتاجه من خلال أسترة حمض الساليسيليك والميثانول. التقطير التفاعلي، الذي يجمع بين حركية التفاعل وعمليات الفصل معًا في نفس الوعاء، يمكن اعتباره أسلوبًا فعالاً للغاية. وبتطبيق متغيرات مختلفة باستخدام برنامج محاكاة العمليات الكيميائية تم تحديد أفضل ظروف التشغيل لتكوين ميثيل الساليسيلات بما في ذلك درجة الحرارة ونوع العمود. يتم إجراء البحث هنا بهدف تقييم أداء العمليات الدفعية (CBD) وشبه الدفعة (SBD) للتقطير التفاعلي وتحديد معدلات التحويل بالإضافة إلى كفاءات التحويل. يتم تسهيل إنجاز محاكاة عملية الإنتاج بواسطة برنامج المحاكاة gPROMS Module Builder الذي يمكنه تصميم أكثر من تفاعلات بسيطة لإنتاج ساليسيلات الميثيل عالية النقاء من خلال التقطير. يقارن هذا البحث أيضًا كفاءة الانتاج. اظهرت طريقة SBD معدل تحويل 85% ولها أعلى درجة نقاء تبلغ 99%.

توفر الرؤى المستمدة من المحاكاة إرشادات قيمة لتحسين كفاءة العملية واختيار وضع التقطير الأنسب للإنتاج على نطاق صناعي. يساهم هذا البحث في الجهود المستمرة لتكثيف العملية ويؤكد على إمكانية التقطير التفاعلي كطريقة قابلة للتطبيق لانتاج ميثيل ساليسيلات.

## 1. Introduction

Methyl salicylate, commonly known as oil of wintergreen, is a plant-derived compound with a variety of roles in plant physiology and applications in agriculture and other industries [1]. Methyl salicylate is widely available as a component in many brands of creams, ointments, lotions, liniments and medicated oils intended for topical application to relieve musculoskeletal aches and pains. Methyl Salicylate is one of the important fine chemical raw materials. It is mainly used as an organic synthesis intermediate and commonly used in many industrials such as resin cleaners, heavy duty hand cleaners, gear and rolling oils, plasticizers in polymer industries, flavors, plastics, green solvents, perfumes, and pharmaceutical and food industries [2]. It is manufactured through esterification of salicylic acid with methanol. Conventional production methods often face challenges such as equilibrium limitations and the need for excess reactants to drive the reaction to completion. These challenges can be effectively addressed using reactive distillation, a process that combines chemical reaction and separation in a single unit, enhancing both conversion and selectivity.

Reactive distillation is considered as one of the effective separation methods, which finds its application in several industries due to the following advantages: high conversion rate, low energy efficiency, and low cost of construction. Reactive distillation was first thought by Backhaus in the year 1932; but, it has caught much importance for the industrial uses in the recent decades mainly because of the coming up of the improved methods of simulation and modeling [3].

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

Reactive distillation commonly abbreviated as RDF refers to the synthesis of a reaction as well as a distillation process both occurring within a single distillation column. This integration has a number of advantages over conventional process which are the introduction of a new category of reactor including the Microreactors and the fluidized bed reactors having enhanced features in relation to mass transfer and reaction rate, the introduction of new separation methods such as the membrane separation and extractive distillation that may enhance the selectivity of the reaction and the introduction of new control strategy which may enhance the efficiency and the operability of RD processes. RD has been applied in many reactions among them are the esterification process, hydration process, etherification process, and polymerization process. Over the past few years, the focus has shifted toward the use of more sophisticated processes, known as advanced reactive distillation technologies (ARDTs), which work to enhance the operation of existing RD processes [4, 5].

This was compounded by the fact that some of the most recent studies in the field are mainly focused on the design aspects of the reactive distillation unit as well as its working conditions.

These parameters include deciding the appropriate number of stages in the reactor, identification of the correct position with which the reactants should be fed into the reactor, and in case of homogeneously catalyzed reactions; the type of catalyst in the liquid phase. The literature also discusses the active section in the column if the reaction is heterogeneous catalyzed as well as the adequate reflux fraction. In the study that was conducted recently, the new approach of solving the problem of optimizing the design and operation of a complex reactive distillation process was presented [6].

Hydrogenation and reactive distillation have been investigated and the actuality proved that the enhancement in methyl salicylate production is possible. For instance, Hua et al [7] conducted experiments in order to evaluate the applicability of transesterification using reactive distillation and obtained high yields and purity levels as contrasted to the standard practice.

This useful technology is now becoming used for the manufacture of fine chemicals to that of bulk chemicals for all operations. The uses of RD include manufacture of esters, ethers, alcohols, and other functional derivatives; synthesis of hydrocarbons including Aviation Fuel, Synthetic Crude Oil and Kerosene; processes like transesterification, esterification, hydrolysis, etherification hydrogenation, and dehydrogenation; alkylation, isomerization; metathesis and disproportionation including wet sulfuric acid process (WSA) process and hydration [8].

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

Essentially, RD implies that the chemical reactor is what does the job of a technical separator. It has been deemed vital by the chemical engineering society, the merging of such two significant functions for the improvement of the process performance. The product does not require an additional distillation of the products and reagents, which means that, firstly, energy (for heating) and, secondly, substances are saved [8]. This separation process is particularly attractive and useful for reactions that are at equilibrium. Thus, it can be suitable for the disproportionate reactions because it does not provide ways of limitations of conversion and phase equilibrium. It is important to understand that the rate of conversion can be boosted significantly higher than the nominal levels stipulated by the equilibrium due to the constant elimination of reaction products out of the active zone [9]. This assists in the lowering of capital and investment costs and this process might be valuable for sustainable development as a result of its reduction on resource use.

It is important to point out that another significant take off realized in the context of RD technologies is the concept of catalytic distillation (CD). The CD is a subcategory of RD in which a catalyst enhances the reaction, only. The catalyst makes the reaction rate faster due to which three different things namely productivity can be improved and selectivity can also be brought in. The latest trends in this area of research are mainly confined to focusing on the shell–tube arrangement of the reactive distillation unit and the associated operating conditions. The following parameters may include deciding the number of required stages, the place of feed of the reactants, and possibly the homogeneously catalyzed liquid if any in some cases. Furthermore, there is also need to determine the reactive zone within the column if the column capable of being heterogeneously catalyzed and the optimal reflux ratio.

The production of methyl salicylate has been advanced through various methods, including microbial engineering, chemical synthesis, and plant-based pathways. Each approach offers unique advantages and potential applications, from safer industrial processes to enhanced agricultural products. Future research may focus on optimizing these methods for higher yields and exploring new applications of MeSC in different industries [10].

The production of methyl salicylate, a key intermediate in pharmaceuticals, fragrances, and flavors, involves complex multi-step processes with significant energy consumption and potential inefficiency. This study pioneers the use of reactive distillation columns for the synthesis of methyl salicylate, combining reaction and separation in one integrated unit. This approach promises to revolutionize the production process by enhancing operational efficiency, reducing energy use, and reducing the equipment footprint. Using advanced process modeling and simulation tools,

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

specifically gPROMS, reactive distillation parameter optimization was applied to achieve high conversion rates and selectivity under various operational conditions. The main feature of this work lies in the innovative application of reactive distillation to the synthesis of methyl salicylate, providing a comprehensive simulation study elucidating the underlying mechanisms. By addressing the economic and environmental challenges of traditional production methods, this research contributes to significant advances in the field of chemical engineering and process intensification.

## 2. Process Models

Simulations of engineering systems entail applying: mathematical equations to describe a real life system in order to better understand its behavior. The Hexa-hydro-cannabinol (HHC) was useful over the years in getting more of the desired design and to understand the dynamic characteristics of the systems. According to Mujtaba [9], the decision in the complexity of the model can be as a result of the numerical methods that are available for solving the systems of equations. These models are outlined in detail as follows in this thesis Just to give a general outlook over the models discussed in the thesis. However, in this thesis, the rigorous model equation with the chemical reaction will be described and analyzed for various of the batch distillation arrangements.

The dynamic optimization problem is converted to a nonlinear programming problem (NLP) and solved by Control Vector Parameterization (CVP) method using efficient SQP-based technique (Mujtaba, 2004) within gPROMS software (general PROcess Modelling System, 2017). The optimization study included reflux ratios, SF-SBD feed rates for pure acrylic acid, which were previously estimated using the CVP method [11]. A comprehensive dynamic model of each column process is integrated into the optimization system.

### 2.1. Column Designs

The column specifications are given below:

- Each configuration consists of an 8-plate setup without reboiler and condenser.
- Condenser steam load: 2.5 kmol/hour.
- The column stages are numbered from highest to lowest, with the reaction zone located in panels 3 to 7, the rectifying zone located above the reaction zone in panels 8 to 10, and the stripping zone located below the reaction zone in panels 1 to 2.
- Synthesis of MeSC catalyzed by the cation exchange resin (Dowex 50).

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

- Initial conditions: Column hold-up (4% of the input size).
- Operating conditions: Operating times (shortest possible time).
- Optimization study parameters: (Reflux rates and SF-SBD feed rates for pure acrylic acid.

### 2.2. Assumptions of Process Model

In order to simplify the complex system and make the modeling process manageable, some assumptions have been made as given below:

- No vapor holdup.
- The reflux drum and trays have a buildup of molar material.
- The process is adiabatic (all heat generated by chemical reactions or absorbed due to endothermic reactions remains within the system, and no heat is lost or gained from the external environment).
- Mixing of liquid at each phase is optimal.
- Rapid energy changes and complete condensation without any sub-cooling.
- Methodology: The CVP method is used to estimate the feed rates of SF-SBD.
- Limitations: Mass equilibrium constraints, energy balance constraints, comprehensive ingredient and material balances, product quality specifications, and equipment size limitations.
- Objective function: Performance goal (for example, maximizing yield or purity), and minimizing the time consumed. [11]

### 2.3. Data Entry

- Reactant flow rates (salicylic acid and methanol).
- Initial concentrations of reactants and products
- Temperature and pressure conditions
- Kinetic parameters of the esterification reaction
- Heat capacities, enthalpy and other thermodynamic properties of ingredients
- Physical properties of column internals (e.g. plate efficiency, resilience, pressure drop).

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

# 3. Reactive Distillation Column

## 3.1. Conventional Batch Distillation

Fig. (**1**) shows the production process of methyl salicylate. The following are the main assumptions taken into account in this process:

- The molar holdup constant on plates and in the condenser.
- Optimal combining on platters
- Fast energy dynamics.
- A constant operating pressure.
- Total condensation without sub-cooling.
- No azeotrope formation.
- The vapor-liquid equilibrium is constant (there are no deviations from Raoult's law) as the system is ideal.
- The mixture of the feed occurs at bubble point temperature.

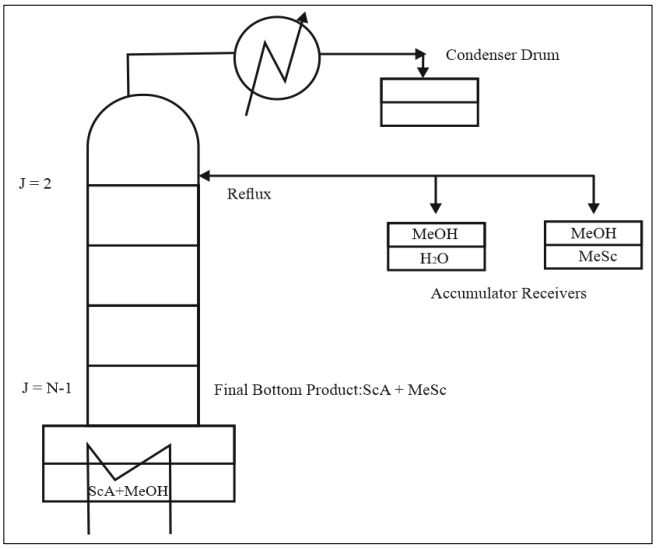


**Fig. (1):** Methanol with salicylic acid esterification process

The equations for the condenser, accumulator, plates, and reboiler are listed below (Equation (1-12) where *j* refers to plates and *i* refers to components.

*Condenser System and Distillate Tank: j=1*

- Accumulator Tank Mass Balance:

(1)

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

$$\frac{dH_{\mathrm{a}}}{dt} = D$$

- Component Mass Balance:

a) Distillate Receiver:

$$H_a \frac{dx_{\mathrm{ai}}}{dt} = D(\mathrm{x_{Di}} - \mathrm{x}_{ai}) \tag{2}$$

b) Reflux Drum Holdup:

$$H_c \frac{\mathrm{dx_{ci}}}{\mathrm{dt}} = \mathrm{V_C y_2} - (\mathrm{V_C} + \Delta \mathrm{n_1 H}_c)\mathrm{X_{Di}} + \mathrm{r_{1i} H_c} \tag{3}$$

- Energy Balance:

$$0 = \mathrm{V_C H_2^V} - (\mathrm{V_C} + \Delta \mathrm{n_1 H}_c)H_1^L - \mathrm{Q_c} \tag{4}$$

*Intermediate plates: j= 2 to N-1*

- Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j \tag{5}$$

- Component Balance:

$$H_j \frac{\mathrm{dx_j}}{\mathrm{dt}} = L_{\mathrm{j-1}} x_{\mathrm{j-1}} + V_{\mathrm{j+1}}\, \mathrm{y_{j+1}} - L_{\mathrm{j}} \mathrm{x_j} - V_{\mathrm{j}} \mathrm{y_j} + H_{\mathrm{j}} \mathrm{r_{ji}} \tag{6}$$

- Energy Balance:

$$0 = L_{\mathrm{j-1}} H_{\mathrm{j-1}}^{\mathrm{L}} + V_{\mathrm{j+1}} H_{\mathrm{j+1}}^{\mathrm{V}} - L_{\mathrm{j}} H_{\mathrm{j}}^{\mathrm{L}} - V_{\mathrm{j}} H_j^{\mathrm{V}} \tag{7}$$

- Equilibrium:

$$K_{\mathrm{j,i}} = \frac{\mathrm{y_{j,i}}}{\mathrm{x_{j,i}}} \tag{8}$$

- Summation:

$$\sum \mathrm{y}_{\mathrm{j,i}} = 1 \tag{9}$$

*Partial Reboiler: j= N*

- Total Mass Balance:

$$\frac{dH_{\mathrm{n}}}{dt} = L_{\mathrm{n-1}} - V_{\mathrm{n}} + \Delta n_{\mathrm{n}} H_{\mathrm{n}} \tag{10}$$

- Component Mass Balance:

$$H_{\mathrm{n}} \frac{dx_n}{dt} = L_{\mathrm{n-1}}(\mathrm{x_{n-1}} - \mathrm{x_n}) - V_{\mathrm{n}}(\mathrm{y_n} - \mathrm{x_n}) + H_{\mathrm{n}} \mathrm{r_n} \tag{11}$$

- Energy balance:

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

$$0 = L_{n-1}(H^{L}_{n-1} - H^{L}_{n}) - V_{n}(H^{V}_{n-1} - H^{L}_{n}) + Q_{r} \quad (12)$$

Equations (1-12) are identical to the other equations for the reboiler, except that N replaces j. This work examines a variety of case studies that utilize batch reactive distillation columns, including the hydrolysis of methyl lactate, ethanol esterification systems, and methanol. Additionally, it examines various optimization problem formulations.

### 3.2. Semi-batch Distillation Columns

The model equation for the intermediate plates referring to the scheme of a typical plate can be presented as follows:

The model equations for SF-SBD operation will be same as those in the CBD column mathematical model shown above except that the extra charged feed ($F_{SaAc}$) terms to the column plates equations (Equation (13) -(16)) will be added.

*Internal Plates j= 1 to N (N, Intermediate Plates)*

Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_{j} - V_{j} + F + \Delta n_{j} H_{j} \quad (13)$$

Component Balance:

$$H_{j}\frac{dx_{j}}{dt} = L_{j-1}x_{j-1} + V_{j+1}y_{j+1} - L_{j}x_{j} - V_{j}y_{j} + Fx_{i} + H_{j}r_{ji} \quad (14)$$

Energy Balance:

$$0 = L_{j-1}H^{L}_{j-1} + V_{j+1}H^{V}_{j+1} - L_{j}H^{L}_{j} + FH_{f} - V_{j}H^{V}_{j} \quad (15)$$

(16)

Relations defining Physical Properties and Chemical Reactions

$$H_{f} = H_{f}(x_{f}, T_{f}, P)$$

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

## 4. Phase Equilibrium and Reaction Kinetics in Esterification

Aqar et al. [1] reported that the kinetics of the methyl salicylate production is catalyzed by a very acidic cation exchange resin. Reversible reaction paths and boiling points (in Kelvin) in the esterification reaction between salicylic acid (ScA) and methanol (MeOH) to produce methyl salicylate (MeSC) and water ($H_2O$) using cation exchange resin (Dowex 50) are shown below (Eq. 17) where the heat of reaction is -133.5 kJ/mol.

| | ScA + | MeOH | ↔ MeSC + | $H_2O$ | (17) |
|---|---|---|---|---|---|
| | Salicylic Acid | Methanol | Methyl Salicylate | Water | |
| Boiling Point (K) | 529.00 | 337.85 | 493.65 | 373.15 | |

Making methyl acrylate requires a Langmuir-Hinshelwood batch process. “Watson" — Hougen (LHHW) activity $\boldsymbol{a_i = x_i \gamma_i}$ the based kinetic model (Eq. 18) was applied [12]:

$$-r_{MeAc} = m_{cat} * 2.67 * 10^{19} \exp\left(\frac{-16248.5}{T}\right) * \left( C_{ScA} C_{MeOH} - 36.85 * 10^{10} \exp\left(\frac{-7797.7}{T}\right) C_{MeSC} C_{H2O} \right) \quad (18)$$

### 4.1. Phase Equilibria (VLE)

Eq. (20) was used to get the equation for the vapor-liquid equilibrium, with the activity coefficient ($\gamma_i$) calculated with the help of the NRTL model. The saturated pressure ($P_i^{sat}$) of components were calculated using Antoine's Eq. (19).

$$\mathrm{Log_{10}} \mathrm{P}_i^{sat} = \mathrm{A} + \frac{\mathrm{B}}{\mathrm{T}} + \mathrm{C} \log_{10} \mathrm{T} + \mathrm{DT} + \mathrm{ET}^2 \quad (19)$$

$$y_i = P_i^{sat} x_i \gamma_i P \quad (20)$$

Where A, B, C, D, and E are the Antoine equation constants as listed in Table (1)**,** T is the temperature in Kelvin. The Antoine constants from Yaws [13]. Aspen Plus software was also used to obtain enthalpy values for all pure components as shown in Table 1. Where the enthalpy of each component was calculated using Eq. (21)

$$\Delta H = \int_{T1}^{T2} Cp \, dT \quad (21)$$

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

**Table (1):** Antoine's equation constants and Enthalpies [13]

| Component | A | B | C | D | E | Enthalpy, H, kJ/kg |
|---|---|---|---|---|---|---|
| Acrylic acid | 177.3858 | $-1.2871*10^{+3}$ | $-5.6301*10^{1}$ | $-1.6667*10^{-7}$ | $1.1353*10^{-5}$ | 211.4 |
| Methanol | 45.6171 | $-3.2447*10^{+3}$ | $-1.3988*10^{+1}$ | $6.6365*10^{-3}$ | $-1.0507*10^{-13}$ | 292.5 |
| Methyl acrylate | 202.6840 | $-1.2160*10^{+4}$ | $-6.6670*10^{+1}$ | $1.8009*10^{-9}$ | $1.806*10^{-5}$ | 222.1 |
| Water | 29.8605 | $-3.1522*10^{+3}$ | $-7.3037*10^{0}$ | $2.4247*10^{-9}$ | $1.8090*10^{-12}$ | 490.14 |

### 4.2. Process Optimization

In this study, the optimization method used is dynamic optimization. This method involves formulating an objective function, such as maximizing yield (Eq. (22)) or minimizing production cost, taking into account a set of differential and algebraic equations that represent the process of reactive distillation. The optimization problem is solved using advanced numerical techniques, such as sequential quadratic programming (SQP) or interior point methods, to find the optimal operating conditions. gPROMS software facilitates this by providing a platform to accurately model the process, integrate governing equations, and perform sensitivity analysis to ensure robust and efficient production. The limit values of all parameters applied in the optimization are listed in Table (2).

$$\text{Maximize } Y_{MSC} = \frac{n_{ScA-out}}{n_{ScA-in}} \quad (22)$$

**Table (2):** Limitation of parameters values used in the optimization

| Parameter | Limits |
|---|---|
| Temperature (K) | 373-393 |
| Reaction time (hr) | 0-1.2 |
| Reactant concentration (mole/hr) | 0-2.5 |
| Product purity (%) | 95-100 |
| Product Yield (%) | 70-100 |

## 5. Results and Discussion

The findings of optimizing the CBD and SF-SBD columns for the top four product concentrations are summarized in Tables (2). These findings were: The optimal reflux ratios, batch processing time, and total energy input that applied in the distillation designs. According to the data in Table 2**Table**, the SF - SBD design outperformed the CBD designs in terms of ester quality. It can be

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

seen from Table (3) that the reflux ratios, batch runs, and energy consumed increased as the MeSC product concentration increased. The highest value of Methyl Salicylate concentration was achieved is 0.995 (mole fraction) by the SF - SBD design while it was 0.778 by the CBD designs.

Increasing the concentration of the MeSC (methyl salicylate) product may require harsh operating conditions to achieve and maintain chemical equilibrium of the reaction. The latter needs high reflux ratios to drive the reaction toward the desired product, requiring a longer batch run time.

In addition, increasing product concentrations can lead to mass transfer limitations and high energy input which is necessary to maintain optimal temperature conditions for both reaction and separation processes.

**Table (3):** Summary of the optimal operating conditions for the CBD and SF-SBD processes

| MeAc purity | MeOH rate (kmol/hr) | Reflux ratio, R | Conversion | Batch time $t_p$, hr | Energy Usage ($Q_{tot}$), GJ |
|---|---|---|---|---|---|
| **CBD column** | | | | | |
| 0.755 | --- | 0.090 | 81.27 | 0.81 | 0.129 |
| 0.765 | --- | 0.100 | 81.27 | 0.83 | 0.133 |
| 0.775 | --- | 0.100 | 81.80 | 0.85 | 0.139 |
| 0.785 | --- | 0.299 | 83.12 | 1.09 | 0.149 |
| **SF-SBD column** | | | | | |
| 0.960 | 0.54 | 0.169 | 84.26 | 1.18 | 0.207 |
| 0.970 | 0.56 | 0.173 | 84.54 | 1.19 | 0.208 |
| 0.980 | 0.57 | 0.176 | 83.93 | 1.21 | 0.208 |
| 0.990 | 1.73 | 0.178 | 85.09 | 1.22 | 0.209 |

### 5.1. Temperature profiles

The constant vessel temperature profiles for methyl salicylate formation in batch reaction distillation are shown in Fig. (**2**). These profiles are essential for understanding the dynamic behavior of the reaction and separation processes within the distillation column. The constant vessel temperature, which is the temperature at the bottom of the distillation column where the liquid mixture is located, provides insight into the progress of the esterification reaction and the separation efficiency.

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

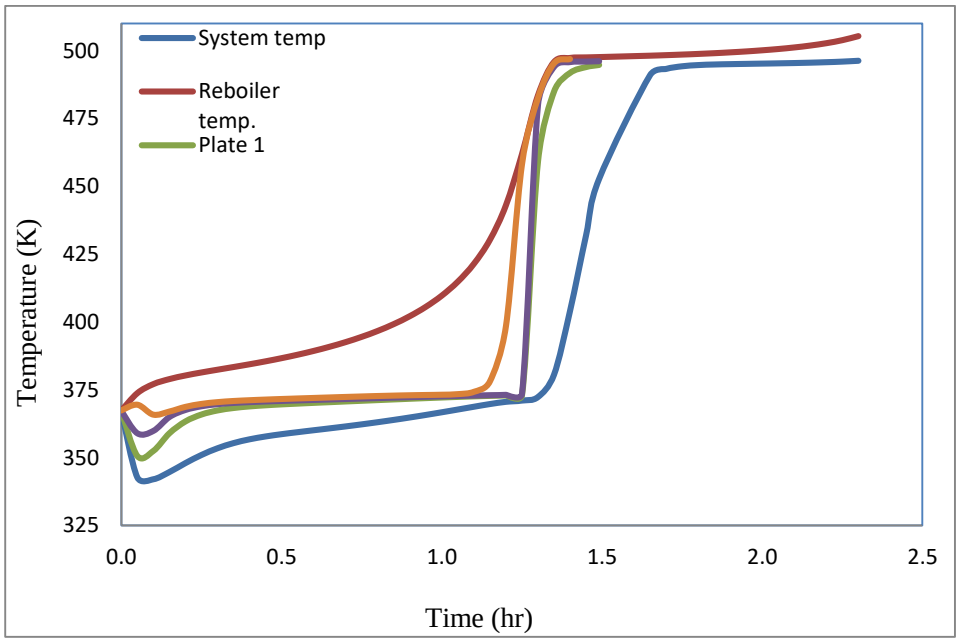


**Fig. (2):** The temperature profiles for methyl salicylate production in CBD system.

At the beginning of the batching process, the temperature of the still vessel rises as the mixture of methanol and salicylic acid is heated. The initial increase in temperature is due primarily to heating of the reactants. When the temperature approaches the boiling point of methanol (about 64.7°C), the methanol begins to evaporate and rise through the column.

As the esterification reaction between methanol and salicylic acid continues, methyl salicylate and water are formed. The temperature in the still vessel continues to rise due to the exothermic nature of the reaction and the removal of methanol through distillation. The presence of a catalyst can speed up the reaction, resulting in a rapid increase in temperature. In the present study, the esterification reaction between methanol and salicylic acid to produce methyl salicylate and water is characterized by a high still pot temperature, driven by the exothermic nature of the reaction and distillation-induced methanol removal. The introduction of a catalyst speeds up the reaction, resulting in a faster rise in temperature. This is in line with the findings of Hua Shi et al. (2010), where the use of acidic Brønsted ionic liquids as catalysts in microwave-accelerated esterification of salicylic acid also significantly increased reaction rates [7, 14]. Both studies highlight the critical role of catalysts in optimizing reaction kinetics and temperature management, although the former focuses on a traditional reactive distillation setup while the latter explores the novel application of microwave technology and ionic liquid catalysts to esterification.

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

### 5.2. Concentration profiles

Fig. (**3**) and Fig. (**4**) show the concentration profiles over time for the accumulator and reboiler tanks, respectively, during the batch reactive distillation process used to produce methyl salicylate.

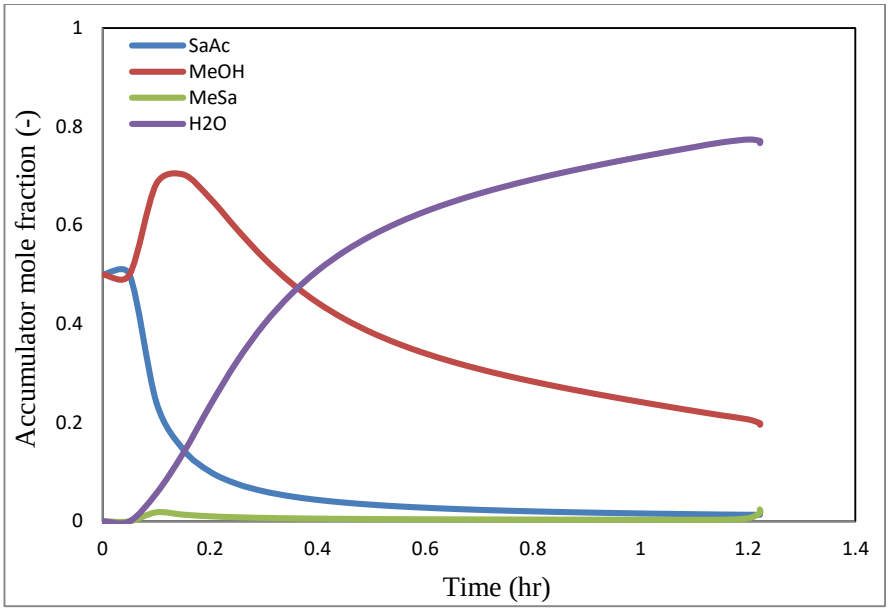


**Fig. (3):** The accumulator composition profiles

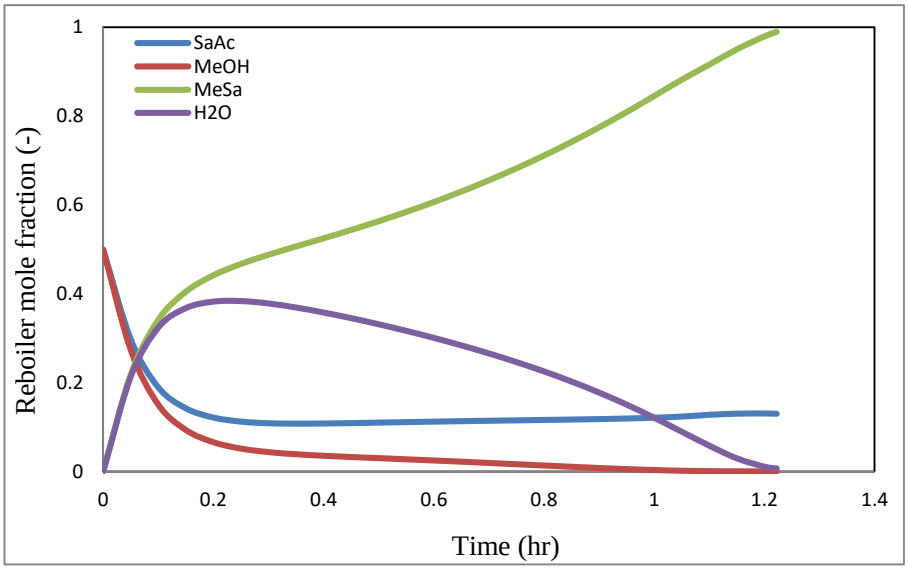


**Fig. (4):** The reboiler composition profiles

Fig. (**3**) demonstrates the dynamics of the process showing how the composition of methyl salicylate and other components of the substance changes in the accumulator during the batch process. At the beginning of the reaction, the energy is high because there is a large amount of reactants; and at the end of the reaction it is low because the product methyl salicylate and accumulates in the solution. The concentration changes are presented in the case of the reboiler tank as seen in the Fig. (**4**) below.

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

As time goes on, the concentration of the reactants in the reboiler, decreases, while the concentration of the methyl salicylate increases which represents an indication of the reaction that was analyzed and distilled.

Together, these numbers provide insight into the efficiency and effectiveness of the reactive distillation process in producing high-purity methyl salicylate. The thermodynamics of liquid-solution behavior models that will be use are based on the concept of local composition. In a liquid solution, it is assumed that local compositions, contribute to the short-range arrangement and specific molecular alignments arising from variations in molecular size and intermolecular forces [7, 14].

### 5.3. Conversion and purity of Methyl Salicate

Fig. (**5**) provides a visual representation of the progress of conversion of reactants to methyl salicylate over the reaction time in the batch reactive distillation process. This type of diagram is crucial for understanding the kinetics and efficiency of the reaction under the specific conditions being studied.

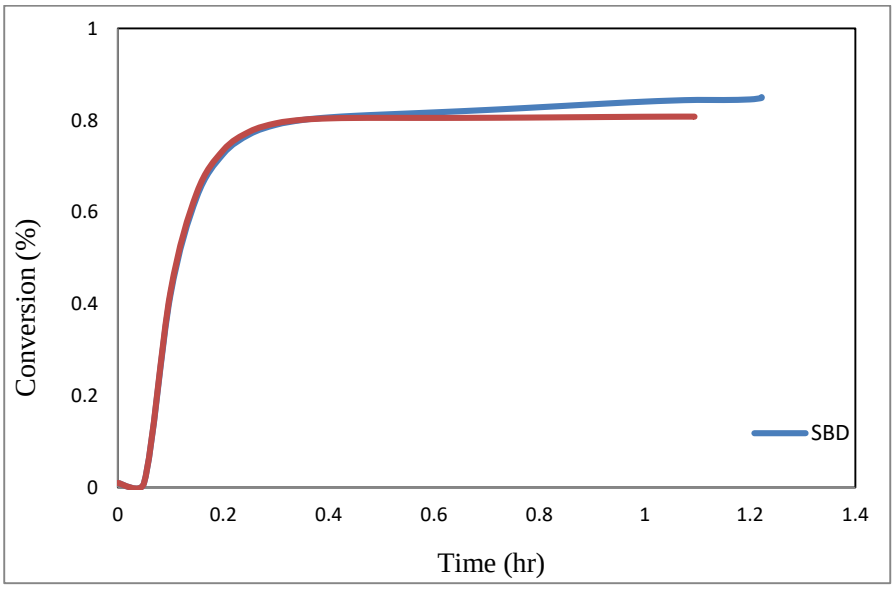


**Fig. (5):** Product conversion versus reaction time

The curve plotted on the graph shows how the conversion ratio changes as the reaction progresses over time. Initially, the conversion rate may be slow due to the low concentration of products and high concentration of reactants. As the reaction proceeds, the rate usually increases until it begins to stabilize near equilibrium.

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

At early periods of the reaction, that is up to 0.05 hours in this case, the conversion is also low and this phase may reveal a constant increase as the reactants start reacting. A steep slope on the linear part (0.05-0.3hr) means that it takes less time for the reaction to reach completion, thanks to the desirable temperature and catalyst concentration. Extensions of the curve lower than the horizontal cutting at 0 hr (zero hour) but above 0.3 hr, suggesting that the rate of conversion may be slowing down because the reactants may be depleted or the reaction may have reached equilibrium.

In a batch of reactive distillation, separation occurs simultaneously with the reaction of products and substances that did not participate in the reaction. This can help in the driving of the process by constantly withdrawing the product methyl salicylate from the reaction mixture hence favoring formation of more products since the system will be trying to counter act the loss according to Le Chatelier's principle.

The nature and the manner of changes in the conversion curve offers an indication of the effectiveness and this reactive distillation process. For instance, a spike accompanied by a level may suggest that the factors influencing the reaction rate such as three factors are favourable for fast conversion. Any deviation or abnormality in the curve predicts can throw a light on issues like abnormalities, side reactions, under optimal conditions and mass transfer limitations.

Fig. (**6**) presents the dependency of the conversion rates on time which is shown for both the batch and semi-batch reactive distillation processes for methyl salicylate synthesis.

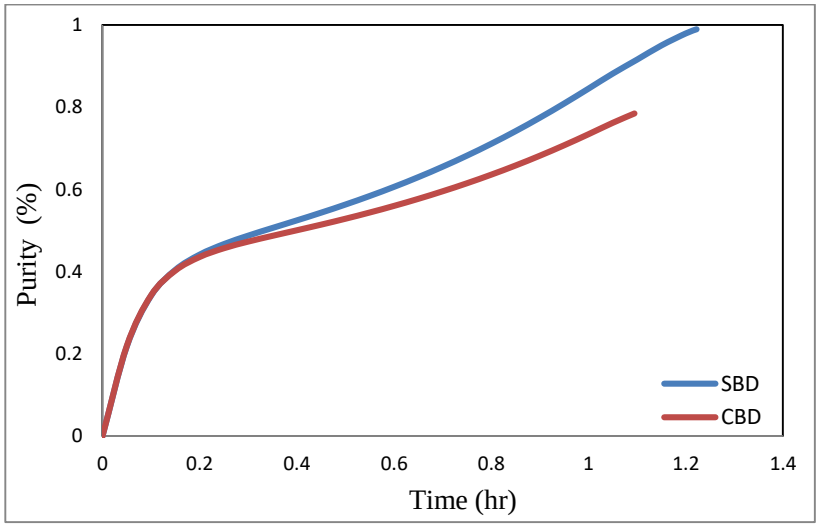


**Fig. (6):** Product purity versus progress time

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

The semi-batch approach usually shows a higher conversion rate (85%) compared to the batch method (80%). This tolerance arises from the ability of the semi-batch process to carefully regulate the addition of reactants and removal of products, thus maintaining reaction equilibrium more effectively. Furthermore, the semi-batch mode provides enhanced control over reaction kinetics and thermodynamics, which may lead to increased yield and purity of methyl salicylate.

As the prior discussion shows, the insights from Fig. (**6**) are useful to determine the best setting in batch or semi-batch manner. Such strategies as retuning response times, adaptive temperature ranges, and varying feed rates provided within the context of semi-batch systems greatly affect the overall efficiency of a process. Therefore, in order to confirm the efficacy of each reactive distillation mode in the context of methyl salicylate synthesis and to contribute more effectively to the identification of the most efficient mode for large-scale implementation, the present study also provides the comparative conversion rates. This differentiation is important to examine the relationships between process complexity and speed, and it will help when deciding on processes' development and setup as well as other operational factors.

Overall, when comparing the results of your study with those reported in the literature [2,5,7], it is clear that both address the exothermic nature of the esterification reaction between methanol and salicylic acid, leading to the formation of methyl salicylate and water. However, our study highlights the continuous temperature rise in the still vessel due to the exothermic reaction and continuous removal of methanol through distillation. This effect is greatly accelerated by the presence of a catalyst, which facilitates a faster temperature increase. In contrast, Lee et al. Focus on optimizing the synthesis process through reactive distillation by simulating different operating conditions to enhance efficiency and selectivity. Their study emphasizes optimizing temperature, reflux ratio and catalyst effects in a more controlled manner to maximize conversion rates and reduce energy consumption. While both studies acknowledge the exothermic effect of the reaction and the presence of the catalyst, your work provides a detailed observation of the real-time temperature dynamics and methanol removal, whereas Hua et al. [7] providing a broader optimal framework for the reactive distillation process.

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

## 6. Conclusions

In this industrial simulation study of methyl salicylate production by reactive distillation, several key results and implications are demonstrated, confirming the feasibility and effectiveness of these industrial applications. Through careful modeling, we studied the effect of various factors such as temperature and column design on the efficient production of methyl salicylate. Comparative analysis between batch and semi-batch reactive distillation processes revealed significantly higher conversions (85%) achievable using the latter, demonstrating the potential of the qualified semi-batch medical distillation technology. This method allows for the continuous addition of reactants and removal of product, which is essential to maintain reaction equilibrium and achieve high conversion rates. The semi-batch reactive distillation process provides superior control over kinetic behavior and thermodynamics, resulting in improved product quality (99%). This confirms their potential as a robust and versatile means of producing methyl salicylate, with implications for quality assurance and downstream processing. By improving the efficiency of reactive distillation columns in methyl salicylate production, our study provides valuable insights for industrial-scale implementation. These insights can guide decision-making processes related to technology adoption and process improvement, ultimately leading to more sustainable and cost-effective practices.

This study reaffirms the feasibility of reactive distillation for the production of methyl salicylate, paving the way for more efficient and sustainable processes in the pharmaceutical, flavor and fragrance industries. Through ongoing research and development, Reactive Distillation stands poised to meet the growing demand for methyl salicylate and other valuable ingredients, driving innovation in manufacturing practices.

### Nomenclature and Abbreviation

| | | |
|---|---|---|
| AAD | Average Absolute Deviation | |
| SaAc | Salicylic Acid | |
| CBD | Convectional batch distillation | |
| D | Distillate flow rate | (kmol/hr) |
| DAEs | Differential algebraic equations | |
| DF-SBD | Double Semi-Batch Distillation | |
| gPROMS | General Process Modelling System | |
| $H_2O$ | Water | |
| $H_a$, $H_c$ | Accumulator and condenser holdup | (kmol) |
| $H_L$, $H_V$ | Liquid and vapour enthalpy respectively | (kJ/kmol) |

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

| | | |
|---|---|---|
| $k_e$ | Pre-exponential factor for the esterification | |
| MeSa | Methyl Salicylate | |
| MeOH | Methanol | |
| N | Number of column plates | |
| $n_c$ | Number of components | |
| P | Operating pressure | (mmHg) |
| $Q_C$, $Q_{Heat}$ | Condenser or reboiler duty | (kJ/hr) |
| r | Reaction rate | |
| R | Reflux ratio | |
| SF-SBD | Semi-Batch Distillation | |
| T | Temperature | (K) |
| $t_p$ | Batch time | |
| V | Vapour flow rate in the column | |
| x, y | Liquid or vapour composition | (mole fraction) |
| $x_a$ | Accumulated distillate composition | (mole fraction) |
| $x_D$ | Instant distillate domposition | (mole fraction) |
| | Superscripts and subscripts | |
| I | Component number | |
| J | Stage number | |
| Λi | Activity coefficient of component *i* | |
| Δn | Change in moles due to chemical reaction | |

Open Access
Vol. 15, No. 2, June 2025, pp. 106-125
P- ISSN: 2220-5381
E- ISSN: 2710-1096

## References

[1] D. Y. Aqar, N. Rahmanian, and I. M. Mujtaba, "A novel split-reflux policy in batch reactive distillation for the optimum synthesis of a number of methyl esters", *Separation Purification Technology*, vol. 221, pp. 363-377, 2019. https://doi.org/10.1016/j.seppur.2019.03.071.

[2] S. R. Kirumakki, N. Nagaraju, K. Murthy, and S. Narayanan, "Esterification of salicylic acid over zeolites using dimethyl carbonate", *Applied Catalysis A: General*, vol. 226, no. 1-2, pp. 175-182, 2002. https://doi.org/10.1016/S0926-860X(01)00900-0

[3] W. Backhouse, "The concept of reactive distillation", *Chemical Engineering Journal*, vol. 22, pp. 466-472, 1932.

[4] J. G. Segovia-Hernández, S. Hernandez, and A. B. Petriciolet, "Reactive Distillation: A Review of Optimal Design Using Deterministic and Stochastic Techniques", *Chemical Engineering and Processing: Process Intensification*, vol. 97, pp. 134-143, 2015. https://doi.org/10.1016/j.cep.2015.09.004

[5] H. Lee, S. Kim, and Y. Park, "Optimization of methyl salicylate synthesis by reactive distillation: a simulation study", *Journal of Process Engineering*, vol. 45, pp. 789-798, 2020.

[6] A. Tsatse, S. R. G. Oudenhoven, A. J. B. T. Kate, and E. Sorensen, "Optimal design and operation of reactive distillation systems based on a superstructure methodology", *Chemical Engineering Research and Design*, vol. 170, pp. 107-133. 2021. https://doi.org/10.1016/j.cherd.2021.03.017

[7] H. Shi, W. Zhu, H. Li, H. Liu, M. Zhang, Y. Yan, and Z. Wang, "Microwave-accelerated esterification of salicylic acid using Brönsted acidic ionic liquids as catalysts", *Catalysis Communications*, vol. 11, no. 7, pp. 588-591, 2010. https://doi.org/10.1016/j.catcom.2009.12.025

[8] J. G. Segovia-Hernández, S. Hernández, and A. B. Petriciolet, "Reactive distillation: A review of optimal design using deterministic and stochastic techniques", *Chemical Engineering and Processing: Process Intensification*, vol. 97, pp. 134-143. 2015. https://doi.org/10.1016/j.cep.2015.09.004

[9] I. M. Mujtaba, "Batch distillation: Design and operation", vol. 3, *World Scientific Publishing Company*, 2004.

[10] T. Chien, D. R. Jones, and T. Danino, "Engineered bacterial production of volatile methyl salicylate", *ACS Synthetic Biology*, vol. 10, no. 1, pp. 204-208, 2020. https://doi.org/10.1021/acssynbio.0c00497

[11] D. Y. Aqar, "Modelling and Optimization of Conventional and Unconventional Batch Reactive Distillation Processes. Investigation of Different Types Batch Reactive Distillation Columns for the Production of a Number of Esters such as Methyl Lactate, Methyl Decanoate, Ethyl Benzoate, and Benzyl Acetate using gPROMS", *(Doctoral dissertation, University of Bradford)*, 2018.

[12] Y. L. Kao, and J. D. Ward, "Simultaneous optimization of the design and operation of batch reactive distillation processes", *Industrial & Engineering Chemistry Research*, vol. 55, no. 1, pp. 267-278, 2016. https://doi.org/10.1021/acs.iecr.5b03170

[13] C. L. Yaws, "Handbook of chemical compound data for process safety", *Elsevier*, 1997.

[14] Y. Ren, M. R. McGillen, V. Daële, J. Casas, and A. Mellouki, "The fate of methyl salicylate in the environment and its role as signal in multitrophic interactions", *Science of The Total Environment*, vol. 749, p. 141406, 2020. https://doi.org/10.1016/j.scitotenv.2020.141406