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Research Article

Thermodynamic Study of One-step Production from Isobutene to Methyl Methacrylate

Lik Quan Lau[1], Sin Yuan Lai[1,2,3,*], Haiyan Li[3], Cheng Loong Ngan[1,3], Mahashanon Arumugam[4], Mukhamad Nurhadi[5]

[1]School of Energy and Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Selangor Darul Ehsan, Malaysia
[2]Kelip-kelip! Center of Excellence for Light Enabling Technologies, School of Energy and Chemical Engineering, Xiamen University Malaysia, Jalan Sunsuria, Bandar Sunsuria, 43900 Sepang, Selangor Dahrul Ehsan, Malaysia
[3]College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, China
[4]Department of Petroleum Technology and Alternative Fuels, Faculty of Environmental Technology, UCT, Prague, Technická 5, 160 00 Praha 6-Dejvice, Czechia.
[5]Department of Chemical Education, Universitas Mulawarman, Kampus Gunung Kelua, Samarinda, 75119, East Kalimantan, Indonesia.

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Abstract

Methyl methacrylate (MMA) has emerged as an essential industrial monomer. However, the toxic by-production and shortage supply of MMA in the global market has gained great attention. Herein, a one-step synthesis to produce MMA from isobutene via a direct oxidative esterification process has been demonstrated to curb the aforementioned downsides. Thermodynamic analysis via Gibbs free energy minimization method proved the feasibility of this route via the equilibrium constant. Despite *tert*-butanol and isobutane showed higher equilibrium constant than isobutene, they should be avoided. Isobutane is highly flammable while the precursor of *tert*-butanol is exorbitant. Thus, isobutene was selected for the equilibrium compositions screening. Isobutene conversion was 90% and 15% MMA yield at 700 °C and IBN: O_2: MeOH ratio with 1:7:1. This route is mainly limited by the generation of side reactions from the reaction of CH_3OH and O_2. By varying the feedstock ratio at 1:2:1, the MMA yield increased to ~25%.

Keywords: Thermodynamic Analysis; Sustainable; One-step Production; Methyl Methacrylate; Isobutene

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1. Introduction

Methyl methacrylate (MMA) is a specialty industrial monomer that is used for the production of poly methyl methacrylate (PMMA) with unique and attractive characteristics that have been utilized in various industries. PMMA is utilized massively in signboards, paint and coating, lighting equipment, and automotive and construction materials due to its superior transparency and excellent weather resistance [1,2]. Making use of its optical characteristics, it has also expanded and grown rapidly in a new field, which is Information Technology (IT), in assembling flat panel displays in recent years. Moreover, PMMA has also been honoured as the queen of resins because of its charming appear-

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* Corresponding Author.
Email: sinyuan.lai@xmu.edu.my (S.Y. Lai);
Telp.: (+60)-3-8705 5124

ance when compared with other synthetic resins [3]. The demand for PMMA has been reported to surpass 2.8 million tons per year, and it is expected to grow constantly with the increment of more than 0.2 million tons every year [4]. Undoubtedly, the high demand for PMMA in the market has boosted the production capacity of MMA, and this has caused the price of bulk MMA to be rose by around 10% annually. In fact, the worldwide demand of MMA overpassed its global supply capacity in 2015 [2]. Also, it has been reported that the global demand of MMA would exceed around 4.8 million metric tons by 2020 where China has been ranked for the largest MMA production and consumption country, and this has made Asia-Pacific become the major market in the world. Next, North America and Europe are ranked as the second and third largest market for MMA, respectively, while the Africa, Latin America and Middle East are also growing fast in producing MMA. This issue has gained attention of numerous researchers from all around the world to investigate the MMA synthetic routes [2].

Ethylene (C_2H_4) which can be obtained from crude oil via steam cracking or fluidized catalytic cracking, is the most common C_2 hydrocarbon used to produce MMA [5,6]. The key step to producing MMA from ethylene is the condensation reaction of formaldehyde with one of the intermediates, which is propanol (propionaldehyde) [1,7]. It is noted that BASF produced MMA from ethylene via the intermediates such as propionaldehyde, MAL and MAA [1]. However, this process possesses disadvantages such as expensive, low yield of product and low single-pass conversion [3,8]. As a result, there was no proclamation of MMA production line using BASF process, and this had given rise to other C_2-based MMA production route — Leading in Methacrylates (LiMA) process. Though the yields of MMA were claimed satisfactory (~90%) under the LiMA process [2], yet this route also suffers from low one-pass conversion and high cost as BASF [1,2], therefore, some breakthrough research is desirable.

Conventionally, MMA is produced via acetone-cyanohydrin (ACH) process, and it is still the most widely used process for MMA production even today [1,9–11]. In 1937, acetone-cyanohydrin process had been first commercialized to produce MMA, and it remained as the only industrial process to produce MMA for 45 years until 1982 [1]. Even until 21st century, this process is still applied by most MMA manufacturers, especially in the market of Europe and North America, which has accounted for around 85% of production capacity worldwide [9,12]. In the ACH process, acetone is used to react with HCN to form acetone cyanohydrin; this latter then reacted with excess concentrated H_2SO_4 to yield methacrylamide sulfate. Then, methacrylamide sulfate was treated with excess aqueous CH_3OH to form mixture of MMA and ammonium bisulphate (NH_4HSO_4) after hydrolyzation and esterification [2,12]. However, this conventional process has suffered from two main drawbacks, which are massive use of toxic reactants, HCN, and environmentally detrimental co-production of NH_4HSO_4 [2,9,12,13]. Hence, this had driven the wish of evolution of alternative process which is much more safe and environmental friendly to produce MMA. By then, a lot of experiments and research using C_2, C_3 and C_4 hydrocarbons as precursors have been widely developed to replace this conventional ACH process [14–16].

Propylene, with the chemical formula of C_3H_6, had derived acetone-cyanohydrin, which was used as feedstock in the conventional ACH process. Hence, the ACH process can be considered as a type of C_3-based MMA production route. Aforementioned, the conventional ACH process has suffered from two main drawbacks, which are massive use of HCN and high-volume generation of NH_4HSO_4 waste. To solve these problems, Mitsubishi Gas Chemical Co., Inc. had developed a new ACH process and commercialized it in 1997 [1,3]. It is claimed that the process has proceeded under atmospheric pressure and temperature of less than 100 °C [17]. Although this process has solved the main problems faced by the conventional ACH process, the large number of reaction steps consume high level of energy. Therefore, it is not feasible in industrial MMA production as this process is not economical. On the other hand, Shell developed a novel attractive MMA production process from propyne in a single-step reaction. As a result, high yield of MMA (99%) obtained, in which 100 kmol of MMA can be produced by per mol of Pd used in an hour, under mild non-corrosive condition at around 50 °C and pressure of carbon monoxide about 1 MPa [18]. Nonetheless, the complication of limited supply of propyne has restricted for commercialization. Propyne which could be obtained as by-products in ethylene plant, can only produce around 1 kiloton in mass per 1000 kilotons ethylene after thermal decomposition of naphtha and ethane [19]. This statistic has protruded the shortage supply of propyne in this MMA production, hence, global demand of MMA is difficult to be fulfilled.

Owing to the environmental issues, low conversion of product, high-energy consumption, cost and supply of raw materials are the general limiting factors as aforementioned, alternative should be explored in leading MMA synthetic process. In the past decade, some Japanese companies such as Mitsubishi Rayon, Japan Methacryl Monomer and Kyodo Monomer have started to develop on C_4-based MMA production route, especially oxidation of isobutene, with the aid of well-designed catalysts [1,3]. This has caused major MMA production capacity in Japan to rely on C_4 routes, even until today. Not only that, but those Japanese companies have also consistently run their overseas plants in some others Asia-Pacific countries like South Korea, Singapore, Thailand and China.

In 2013, production of isobutene (C_4H_8) had been reported to exceed 10 million metric tons per year with wide application in various industries [20,21]. This indicated that there is an adequate supply of isobutene (IBN) in the market. In the MMA production routes, the isobutene oxidation process has gained attraction from numerous researchers to study and commercialize it with the aid of well-designed catalysts [1–3,22–24]. It is a three-step process with the involvement of the intermediates such as methacrolein (MAL) and methacrylic acid (MAA). Historically, the Japanese company, Nippon Shokubai Kagaku Kogyo Co. was the first to propose direct oxidation of isobutene to form MMA [25,26]. On account of that, C_4-based MMA production is a preferable route due to its environmental benignancy [9]. Hence, synthetic routes of MMA from C_4 hydrocarbons have gained great interest and attention from researchers. Given the aspects from the economic and environment, IBN or TBA is favorable among C_4 hydrocarbons as they are cost-efficient and environmental friendly [1,9,10,27]. IBN is generally obtained from dehydration of TBA or catalytic dehydrogenation of isobutane (IBAN).

The C_4 hydrocarbon is one of the byproducts emitted from oil refineries, which could be valorized into valuable products, *i.e.* MMA. By implementing such waste-to-product concept, circular economy and sustainable industry can be advocated. Currently, numerous researchers are focusing on MMA production from C_4 hydrocarbons, especially IBN, via a three-step or two-step process [1–3,9,23,24]. In the process of direct oxidation of isobutene (three-step process): Firstly, isobutene as precursor will undergo oxidation to form methacrolein (MAL); Secondly, oxidation to produce methacrylic acid (MAA); and thirdly esterification to MMA [1]. Figure 1(a) shows the reaction pathways of the three-step MMA synthetic route from isobutene. While for MAL direct oxidative esterifica-

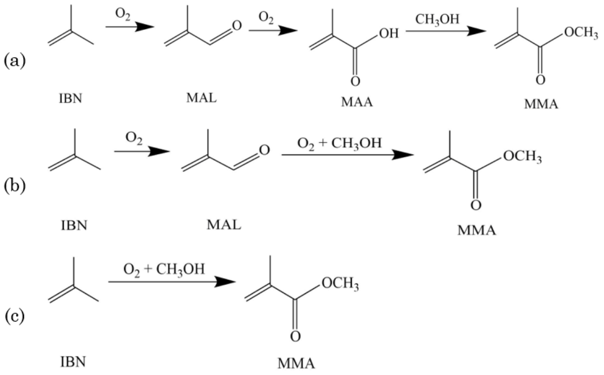


Figure 1. Reaction pathways from IBN to MMA: (a) three-step process, (b) two-step process and [1] (c) one-step process.

Table 1. Below is the summary of the MMA production processes.

Routes	Descriptions	Ref.
C_2	MMA from ethylene is the condensation reaction of formaldehyde with propanol/ propionaldehyde	[5,6]
	MMA from ethylene via the intermediates such as propionaldehyde, MAL and MAA	[1]
	LiMA Process: Aldol condensation to give methacrolein (MAL), then the oxyesterification of MAL with methanol to give MMA.	[2]
C_3	Conventional ACH process	[1]
	New ACH process uses propylene as the feedstock	[1,3]
	The reaction of propyne and CO with Pd as the catalyst	[18]
C_4	Isobutene oxidation to methacrylic acid (MAA)	[1,3]
	Direct oxidation of isobutene to form MMA	[25,26]
	Three-step process: isobutene-to-MAL; MAL-to-MAA; MAA-to-MMA	[1–3,9,23,24]
	Two-step processes: Isobutene-to-MAA; MAA-to-MMA or MAL-to-MAA; MAA-to-MMA	[1–3,9,23,24]

tion process (two-step process), MMA is directly produced after oxidative esterification of MAL and oxidation from isobutene that shown in Figure 1(b). However, the production of MMA from IBN can still be described as less feasible due to various factors such as high energy consumption because of long reactions time (long reaction pathway) and excess usage of methanol (esterification) [13]. The shorter reaction pathway, *i.e.* oxidative esterification of IBN to MMA, is proposed in Figure 1(c). A summary regarding the MMA production process routes are summarized in Table 1.

In order to save energy and prevent the loss of chemicals, thermodynamic analysis was used in this study. However, there is limited literature discuss on the thermodynamic study of methyl methacrylate (MMA) production. Nonetheless, we have found two related studies for comparison and discussion [13,28]. Guan *et al.* [13] has discussed MMA production through C_4 (oxidative esterification of methacrolein (MAL)) and C_3 (aldol condensation of methyl acetate (MeOAc) and formaldehyde). The optimal performance of the oxidation and esterification of MAL is strongly dependent on the molar ratio of MAL/O_2 and MAL/methanol, whilst least effects from the temperature and pressure. The MMA production increases with the concentration of methanol and O_2 [13]. On the other hand, it is found that the temperature range of 350–400 °C and molar ratio of methanol/MeOAc is more than 2 are optimal environment for the aldol-condensation of MeOAc [13]. Another thermodynamic analysis showed that the methacrylate production from propionate with methanol via either dehydrogenation or partial oxidation of methanol-to-formaldehyde pathways [28]. By comparisons, higher propionate conversion and selectivity were observed using methanol dehydrogenation to formaldehyde intermediate. The optimal temperature for both reactions were within the temperature range of 225–250 °C. For the partial oxidation of methanol to formaldehyde, the optimized molar ratio of oxygen/methanol was 0.5 [28]. Same as literature [13], the pressure has negligible effect to the systems.

Thermodynamic analysis shows a clear direction of the possible reactions, thus developing a process to produce MMA from IBN with lesser steps was conducted in this research. To date, the experimental work of IBN-to-MMA using a one-step pathway has not been reported. Herein, this research aims to investigate the feasibility of this direct one-step process using Gibbs free minimization method. The equilibrium constant and equilibrium compositions of the one-step MMA production route were studied. The temperature and feed composition screening on the conversion of IBN to MMA was also investigated.

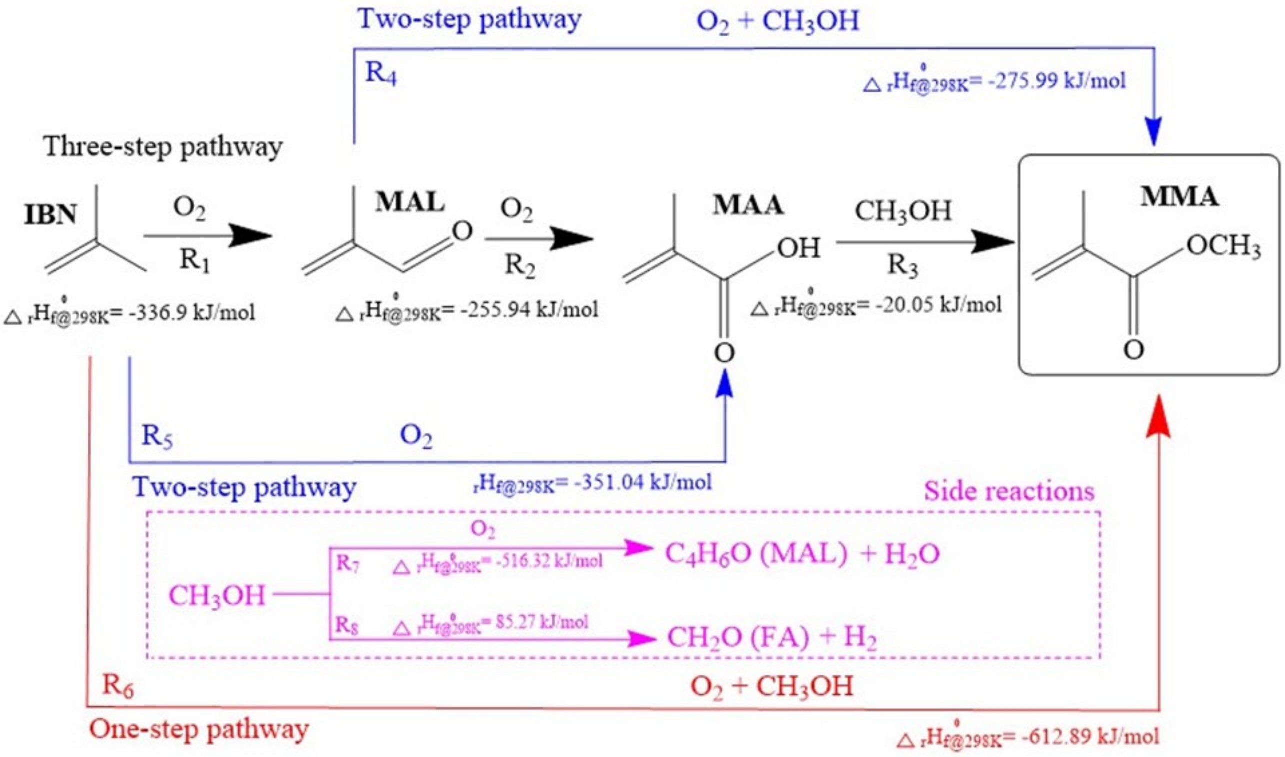


Figure 2. MMA production routes from IBN.

2. Materials and Methods

2.1 Synthetic Routes and Chemical Equations

Different synthetic routes of MMA production with different steps of process steps are displayed in Figure 2. Overall, IBN acts as the precursor to initiating chemical reactions. For the three-step process, IBN undergoes oxidative dehydrogenation to form MAL and H_2O (R1), followed by oxidation to produce MAA (R2) and eventually esterification to synthesize MMA (R3).

Next, the oxidation of MAL (R2) and esterification of MAA (R3) in a three-step process can be replaced with a step of oxidative esterification of MAL to directly produce MMA and H_2O (R4). Therefore, this has made the establishment of the two-step MMA synthetic route. Besides, another reaction pathway for the two-step MMA synthetic route is the direct oxidation of IBN to form MAA (R5), followed by the esterification of MAA to produce MMA (R3). In this two-step MMA synthetic route, H_2O is produced as the by-product. Meanwhile for the one-step process, MMA is directly produced from IBN with the reaction of oxidative esterification, and H_2O is produced as the by-product (R6). At the same time, two side reactions, which are oxidation of methanol to produce MAL and H_2O (R7), as well as dehydrogenation of methanol to produce formaldehyde (FA) and hydrogen (R8), will occur to produce side products in one-step MMA synthetic process. All individual stoichiometry equations (E1 – E8) presented in Figure 2 are assigned to electronic supporting information (ESI).

2.2 Gibbs Free Energy Minimization Method

In order to determine the equilibrium composition of the production reaction system, the Gibbs free energy minimization module was adopted using Aspen Plus software. Generally, the total Gibbs free energy (G_T) of the whole system for component i is the function of temperature and pressure. The details of the calculations are well documented below (Equations (1) – (4)).

$$G_T = \sum_{i=1}^{m} n_i \mu_i = \sum_{i=1}^{m} n_i \mu_i^0 + RT \sum_{i=1}^{m} n_i \ln \frac{f_i}{f_i^0} \quad (1)$$

where, R is universal gas constant (8.314 J/mol.K), T is reaction temperature (K), n_i is mole of component i, and μ_i is chemical potential of component i.

Meanwhile, reaction equilibrium, f_i, can also be calculated using the following equation:

$$f_i = \varphi_i y_i p \quad (2)$$

where φ_i is fugacity of component i, y_i is mole fraction of component i, and p is pressure.

At the same time, the total Gibbs free energy minimization of the entire system is subject to mass balance constraints as follows:

$$\mu_i + \sum_{j=0}^{k} \lambda_i a_{ji} = 0 \quad (3)$$

where λ_i is Lagrange multiplier of component i, and a_{ji} is number of atoms of element j in component i.

Therefore, Equations (1)–(3) can be combined to form Equation (4) as follows:

$$\sum_{i=1}^{m} n_i \left(\mu_i^0 + RT \ln \frac{\varphi_i y_i p}{f_i^0} + \sum_{j=0}^{k} \lambda_i a_{ji} \right) = 0 \quad (4)$$

Consequently, the equilibrium compositions of the entire system based on the chemical reactions stated in ESI (Equations E1 – E8) can be calculated as a function of temperature, pressure, and feedstock composition using the Gibbs free-energy minimization module.

2.3 Determination of Equilibrium Constant

The reference temperature and pressure are set to be 298 K and 1 bar, respectively. Gibbs Free Energy of formation ($G°_{f@298K}$), Entropy of formation ($S°_{f@298K}$) and Enthalpy of formation ($H°_{f@298K}$) are also equated to zero for all components involved in the current study (H_2, H_2O, O_2, CH_2O, CH_3OH, C_4H_8, C_4H_6O, $C_4H_6O_2$, and $C_5H_8O_2$) at gas state. Since atmospheric pressure is commonly practiced in past studies, thus an assumption on the ideal gas state is made for the thermodynamic properties. In short, the temperature effect will be investigated, however, the pressure effect will be neglected in the current study. It is also assumed that all of the reactions are stoichiometric and are described as such in the reaction equations. On this basis, the required thermodynamic properties for the components are retrieved from the Chemical Properties Handbook [29] and tabulated in Table E1 in ESI. The equilibrium constant (K_{eq}) of various synthetic routes of MMA from IBN can be determined according to Equations (5)–(9).

Based on the Equation (5), the Gibbs free energy of reaction, ΔG_{rxn}, of each independent reaction significantly affects magnitude of the equilibrium constant at the corresponding temperature. The $K_{eq} > 1$ indicates forward reaction, which means the products are thermodynamically favourable, while $K_{eq} < 1$ implies reverse reaction.

$$K_{eq} = \exp\left(-\frac{\Delta G_{rxn}}{RT}\right) = \exp\left(-\frac{\sum v_i \Delta G_{fi}^0}{RT}\right) \qquad (5)$$

where, R is universal gas constant (8.314 J/mol.K), T is reaction temperature (K), v_i is stoichiometry of component i, and $\Delta G^0{}_{fi}$ is Gibbs free energy of formation of species i (J/mol).

At the same time, the $\Delta G^0{}_{fi}$ in Equation (5) is computed by Equation (6) through determination of change in Entropy of formation, $\Delta S^0{}_{fi}$ (J/mol.K), and change in Enthalpy of formation, $\Delta H^0{}_{fi}$ (J/mol) for particular component i which are shown in Equations (7) and (8), respectively.

$$\Delta G_{fi}^0 = \Delta H_{fi}^0 - T\Delta S_{fi}^0 \qquad (6)$$

$$\begin{aligned}\Delta S_{fi}^0(T) &= S_{f@298K-i}^0 + \int_{298}^{T} \frac{C_{pi}}{T} dT - R\ln\frac{P}{P_0} \\ &= S_{f@298K-i}^0 + \int_{298}^{T} \frac{C_{pi}}{T} dT - R\ln P\end{aligned} \qquad (7)$$

$$\Delta H_{fi}^0(T) = H_{f@298K-i}^0 + \int_{298}^{T} C_{pi} dT \qquad (8)$$

where, $S^0{}_{f@298K\text{-}i}$ is entropy of formation of component i, $H^0{}_{f@298K\text{-}i}$ enthalpy of formation of component i, C_{pi} is heat capacity of component i (J/mol.K), and P is reaction pressure (1 bar).

Shomate's Equation (9) was used to determine the gas-phase heat capacity of component i at constant pressure and a given temperature. The substance-dependent heat capacity coefficients (A, B, C, D, E) for the components are retrieved from the Chemical Properties Handbook [11] and tabulated in Table 2E of ESI.

$$C_p = A + Bt + Ct^2 + Dt^3 + \frac{E}{t^2}; t = \frac{T(K)}{1000} \qquad (9)$$

3. Results and Discussion

3.1 Feasibility of the Single-step MMA Production Route

3.1.1 MMA production from isobutene

MMA is generally to be produced from IBN via either a three-step process (R1 to R3) or a two-step process (R1 & R4; R5 & R3). To advocate the eco-friendly shorter pathways, a single-step MMA production from IBN (R6) was studied herein. Despite it being an energy-saving single-step process, the coexistence of oxygen and methanol in the feed could generate a side reaction. This side reaction is owing to the oxidation of methanol to produce MAL as well as dehydrogenation of methanol to produce formaldehyde. Figure 2 displays the different MMA production routes from IBN, where the overall routes are divided into 8 individual equations (R1–R8). Thermodynamic calculations were carried out on these routes to analyze the feasibility of the single-step MMA production route from IBN (R6). The chemical species involved in this study are IBN, MAL, MAA, MMA, O_2, H_2, MeOH and FA, where MAL (R7) and FA (R8) are the by-products. The enthalpy of reaction ($\Delta_r H^0{}_{f@298K}$), entropy of reaction ($\Delta_r S^0{}_{f@298K}$) and Gibbs free energy of reaction ($\Delta_r S^0{}_{f@298K}$) for equations R1 – R8 are calculated and tabulated in Table E3 of ESI.

All reactions are exothermic with different negative enthalpy of reactions, except R8 appears as an endothermic reaction with a positive enthalpy of reaction, 85.27 kJ/mol. Next, Gibbs free energy of the reactions was used to determine the spontaneity, where negative and positive values indicate a spontaneous and non-spontaneous reaction, respectively. Similarly, routes R1–R7 are spontaneous chemical reactions with various negative Gibbs free energy of reactions, while only R8 exists as a non-spontaneous chemical reaction with a positive value, 52.60 kJ/mol. This indicates that the side reaction, R8, dehydrogenation of methanol to produce formaldehyde is unlikely to occur, hence, causing less or even zero effect during single-step MMA production from IBN. The aforementioned routes (R1–R8) was simulated at room temperature (25 °C). Meanwhile, the entropy of reactions specify the condition of Gibbs free energy of reactions with the corresponding enthalpy of reactions. The Gibbs free energy of reactions and its corresponding entropy and enthalpy of reactions are tabulated in Table E4.

By comparing the calculated thermodynamic data of routes R1–R7, R6 shows the lowest value of enthalpy and Gibbs free energy of reactions, indicating that R6 is a more feasible route than the three-step process (R1–R3) and two-step process (R1 & R4; R5 & R3). The three-step process (R1–R3) and two-step process (R3 & R5) are mainly limited by esterification of methanol (R3) as it exhibits a nearly positive value of enthalpy and Gibbs free energy of reaction. R7, which is another side reaction of R6, has obtained the second lowest enthalpy of reaction, which might affect the conversion of IBN into MMA. Thus, the low reaction temperature is preferable for the MMA conversion from IBN as R7 is only spontaneous at high temperature. R7 has a negative value of enthalpy but a positive value of entropy, and hence, resulting its corresponding condition of Gibbs free energy of reaction according to Table E4.

Furthermore, reaction equilibrium constant (K_{eq}) for the reactions (R1–R8) were obtained from Gibbs free-energy minimization module (RGIBBS reactor). A graph of ln K_{eq} versus temperature is plotted and displayed in Figure 3. It can be observed that the equilibrium constants for routes R1–R7 lie above the reference line (ln K_{eq} = 0), indicating the feasibility of these reaction routes. These reactions are favored in forward reactions, shifting reactants to products. On the other hand, the side reaction, R8, falls below the reference line, indicating it is not feasible to occur (reverse reaction) and this result agrees well with the statement mentioned earlier. However, it gradually favors the forward reaction when the temperature increases. Figure 3 shows that R5–R7 have exhibited relatively large equilibrium constant, where the single-step MMA production route (R6) has resulted in the largest value of the equilibrium constant among all other equations. Although R1, R2, and R4 have also exhibited large equilibrium constant values, there is still an obvious gap compared to R6. Hence, it further confirmed that the single-step MMA production route, R6, is the most thermodynamically favorable route when compared to the two- or three-step production pathways. However, the side reaction - oxidation of methanol to produce MAL (R7) has a significant effect on single-step MMA production as it has a close equilibrium value. This significant effect can be resolved when the reaction temperature decreases, as can be seen from the Figure 3, that the gap between R6 and R7 is getting bigger when reaction temperature decreases. These results also agrees well with the statement above, where R7 displays less effect than R6 at low reaction temperature.

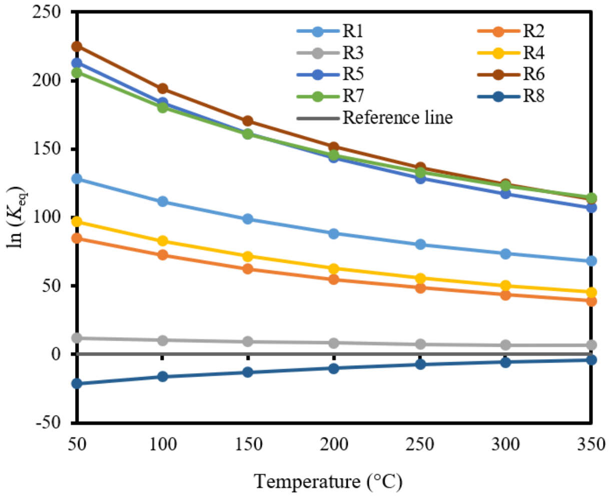


Figure 3. Equilibrium constant as a function of temperature for Equation R1–R8.

Generally, the equilibrium constants for equations R1–R7 decrease when the reaction temperature increases, hence, it is favorable to synthesize MMA from IBN at low temperature or room temperature. Ideally, the production of MMA from IBN should be carried out at a low temperature in order to create an optimum condition for better production. However, the reaction temperature has a less significant influence on the production of MMA from MAA as there is only slight deviation on the graph throughout the experiment temperature displayed in Figure 3. Therefore, precise screening of the operating parameters, including reaction temperature and feed composition, is significant to investigate their influence on the IBN-to-MMA production.

There are other C_4 hydrocarbons, *viz.* isobutane (IBAN) and tert-butanol (TBA), will substitute IBN in order to study their feasibilities in the formation of MMA. Therefore, R1, R5 & R6 with the involvement of IBN will be replaced with A1–A3 for isobutane (IBAN) route and B1–B3 for the tert-butyl alcohol (TBA) route.

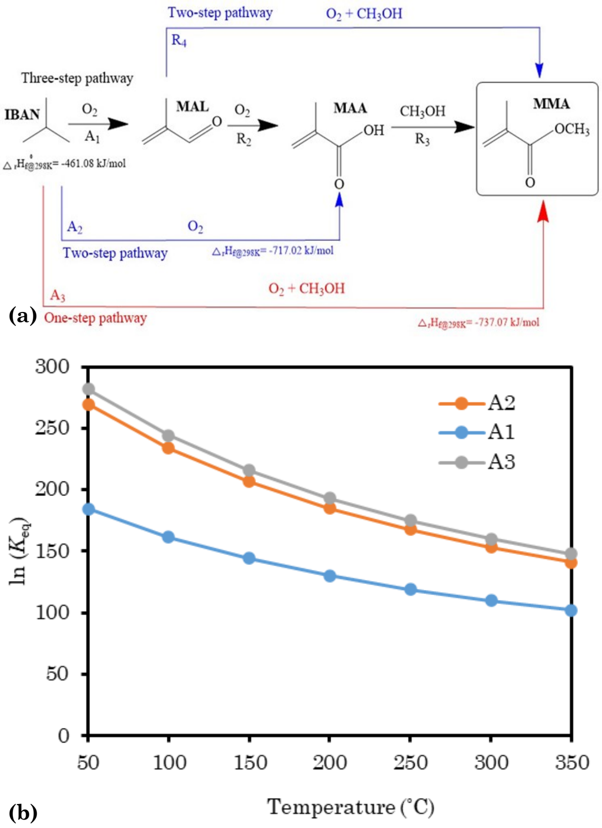


Figure 4. (a) MMA production routes from IBAN; (b) Equilibrium constant as a function of temperature for the routes A1–A3.

3.1.2 MMA production from isobutane (IBAN)

Figure 4(a) displays the reaction routes for several MMA production route from IBAN while Table E5 and Figure 4(b) shows the calculated the thermodynamic data for the routes A1–A3. From the point view of thermodynamic, routes A1–A3 exhibit similar behavior as R1, R5 and R6 as the reactions involved has appeared as exothermic process and classified as spontaneous chemical reactions with negative Gibbs free energy of reaction. Among them, oxidative esterification of IBAN to MMA (A3) is the most feasible reaction pathway due to its lowest value of enthalpy and Gibbs free energy of reaction. This result has proven the high feasibility of the single-step MMA production when compared with two and three-step pathway. In addition, the only difference of thermodynamic behavior between routes A1–A3 with IBN route is that the conditions of Gibbs free energy. As referring to Table E5, routes A1–A3 are spontaneous at all temperature while R5 and R6 are only spontaneous at low temperature. Next, the equilibrium constants that obtained from the simulation as shown in Figure 4(b) has illustrated that routes A1–A3 are forward reactions as they lie above the reference line. The single-step MMA production route from IBAN (A3) has resulted the largest equilibrium constant over the range of reaction temperature. Although A2 has resulted close equilibrium constant with A3, this two-step pathway for MMA is limited by R3 with the unfavorable thermodynamic behavior. As a result, the production or conversion of the desired product in the industry will be unsatisfactory in the point view of thermodynamics. Hence, route A3, the single-step pathway, is the most thermodynamically favorable production route as it exhibits the largest equilibrium constant and lowest value of enthalpy and Gibbs free energy of reaction.

3.1.3 MMA production from tert-butanol (TBA)

TBA, as another candidate for C_4 hydrocarbons, has been studied in this research. Figure 5(a) illustrates the reaction routes for MMA production from TBA and the thermodynamic data for the reaction B1–B3 are tabulated in Table E6 and portrayed in Figure 5(b). Figure 5(a) depicts that the routes B1–B3 with negative values of enthalpy and Gibbs free energy of the reaction. Therefore, they are exothermic and spontaneous reactions; and similarly, they displayed alike thermodynamic behavior as R1, R5 & R6. Then, the calculated results have once again proven that the single-step MMA production route is the most feasible pathway, compared with the two- and three-step pathways. This is because the single-step MMA production route from TBA (B3) exhibited the lowest value of enthalpy and Gibbs free energy of reaction, which are −545.78 kJ/mol and −573.84 kJ/mol, respectively, in comparison with B1 and B2. Next, it also can be noticed that routes B1–B3 are spontaneous at all temperatures and this has made these reactions contrast to R5 and R6, which are only spontaneous at low temperature, in term of thermodynamic behavior. Figure 5(b) portrays the equilibrium constants over a range of temperature (50–350 °C) for B1–B3. All of the equations lie above the reference line indicating the forward reactions with large positive equilibrium constants. As expected, the single-step MMA production pathway (B3) has presented the largest equilibrium constant, comparing with B1 and B2.

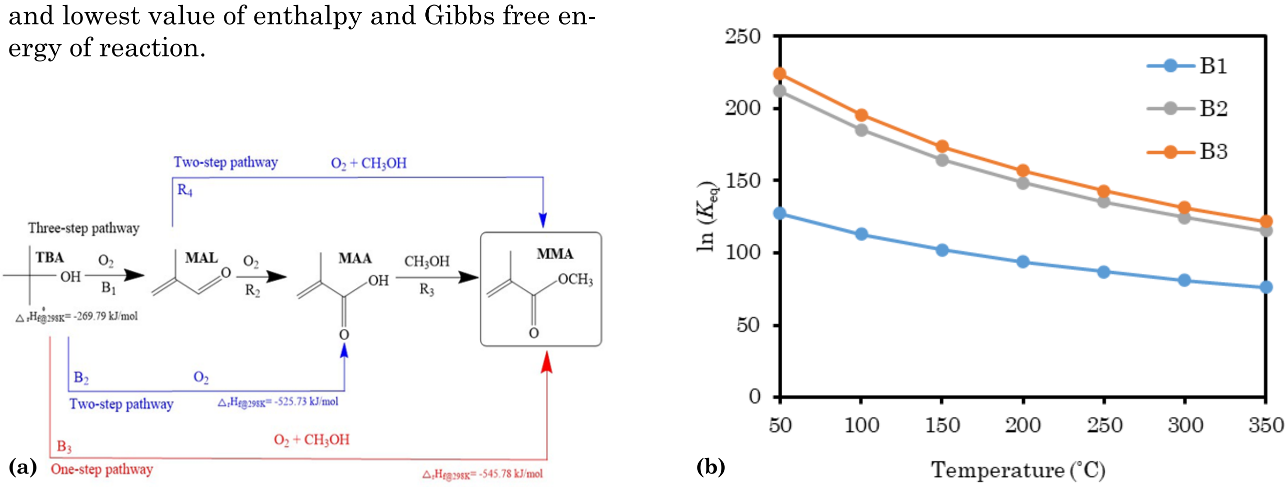


Figure 5. (a) MMA production routes from TBA; (b) Equilibrium constant as a function of temperature for Equation B1–B3.

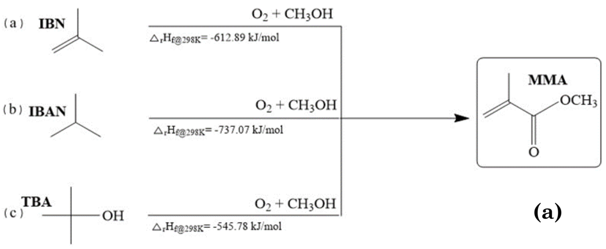
3.1.4 Single-step MMA production from isobutene, isobutane and tert-butanol

In order to ease the visualization and for a better comparison, all of the single-step MMA production route from IBN, IBAN and TBA are illustrated in Figure 6(a). Their corresponding thermodynamic data are tabulated in Table E7. Surprisingly, the single-step MMA production from IBAN has resulted in the lowest enthalpy and Gibbs free energy of reaction among the three routes. The IBAN route with the largest equilibrium constant as shown in Figure 6(b) further proves that the IBAN route will be more thermodynamically favorable. However, IBAN should be avoided reacting with oxygen in order to reduce explosion hazards, thus, limiting its industrial application for this route, A3 [30]. Furthermore, the high flammability of IBAN when exposed to oxygen at room temperature has been confirmed [31]. Hence, the IBAN route will not be preferable in the synthesis of MMA. Next, it can be noticed that IBN has similar thermodynamic behavior with TBA, as they resulted in an almost identical equilibrium constant that displayed in Figure 6(b). In spite of this, TBA is not the preferred option in industries for two reasons. TBA highly relies on propylene oxide as the raw material [2], which was rated as USD 22.5 billion in 2021 and projected with CAGR of 5.6% from 2021 to 2016 [32]. Besides, the alternative route of TBA synthesis, such as IBAN auto-oxidation and hydration of IBN, could incur additional capital costs [2]. Therefore, single-step MMA production from IBN was remained as the research highlight and precise screening and optimization were carried out to achieve highly efficient conversion of IBN into MMA.

3.2 Optimization on the Operating Parameters

3.2.1 Effect of temperature

Temperature screening of the single-step MMA production route from IBN as shown in Equation (10) was conducted over the range from 0 to 900 °C. The screening was carried out with the aid of conversion of reactant, which in this case is IBN, and yield of MMA. The IBN conversion and MMA yield calculation are computed using Equations (11) and (12), respectively, where n is denoted as the number of moles. In the simulation, the feed ratio of reactants (IBN: O_2: MeOH) was input using stoichiometry ratio, 1:1.5:1, and the pressure was set at atmospheric pressure, 1 bar.



$$C_4H_8 + \frac{3}{2}O_2 + CH_3OH \rightarrow C_5H_8O_2 + 2H_2O \tag{10}$$

$$IBN\,conversion = \frac{n_{IBN(initial)} - n_{IBN(final)}}{n_{IBN(initial)}} \times 100\% \tag{11}$$

$$MMA\ yield = \frac{Actual\ yield}{Theoretical\ yield} \times 100\% \tag{12}$$

Both conversion of IBN and yield of MMA remained constant at the maximum rate (100%) over the temperature range due to ideal assumption was adopted. The high performance indicates that this eco-efficient process is highly recommended. Nonetheless, by considering the byproduct formation, the MMA yield accounted for 33%. The equilibrium composition of the reactants and products, which are IBN, O_2, MeOH, MMA, and H_2O, levelled out from 0 to 900 °C. The equilibrium composition of MMA and H_2O remained constant at 33% and 66%, respectively. Moreover, all the reactants were kept constant at 0%, indicating that they were fully converted throughout the temperature range. Hence, it is believed that there are some possible by-products that will be formed during the synthesis of MMA. It has been reported that acetone and some other components were produced during synthesis of MMA from MAL in a single step [27], therefore, by-products, such as acetone (ACE), car-

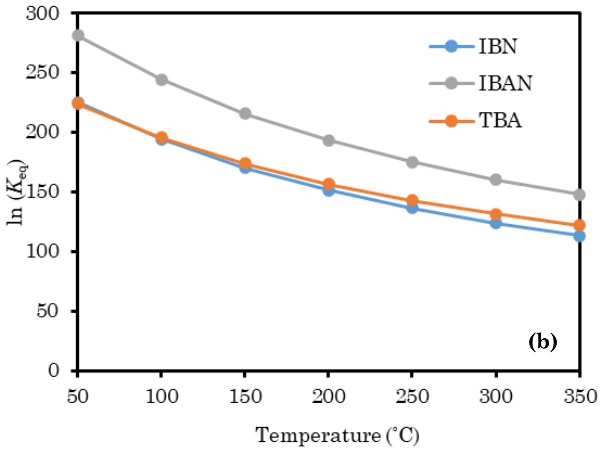


Figure 6. (a) One-step reaction pathways of MMA production from IBN, IBAN, and TBA; (b) The equilibrium constant as a function of temperature for the single-step pathway of MMA.

bon monoxide (CO), and carbon dioxide (CO_2), were taken into account, thus, the single-step MMA production route from IBN with by-products added (R6') is shown as Equation (4):

$$R6': C_4H_8 + 4.5O_2 + 6CH_3OH \rightarrow C_5H_8O_2 + 9H_2O + C_3H_6O + CO_2 + CO \tag{4}$$

Similarly, the temperature screening and equilibrium product composition were carried out on this single-step route with various by-products. The results of the simulation for temperature screening and equilibrium product composition are displayed in Figures 7(a) and (b), respectively. As illustrated in Figure 7(a), the conversion of IBN rose steadily from 10 to 12% when the reaction temperature increased from 0 to 900 °C. For MMA yield, it levelled out at 0% until 300 °C, followed by steep increase of yield (0.2 to 55%) from 300 to 900 °C. Herein, it can be explained that the activation energy for the reactants to convert to the products has been achieved when the reaction temperature reached 300 °C. With the increasing temperature, more heat is supplied to reactants to overcome activation energy, hence causing the steep increase in the MMA yield from 300 to 900 °C.

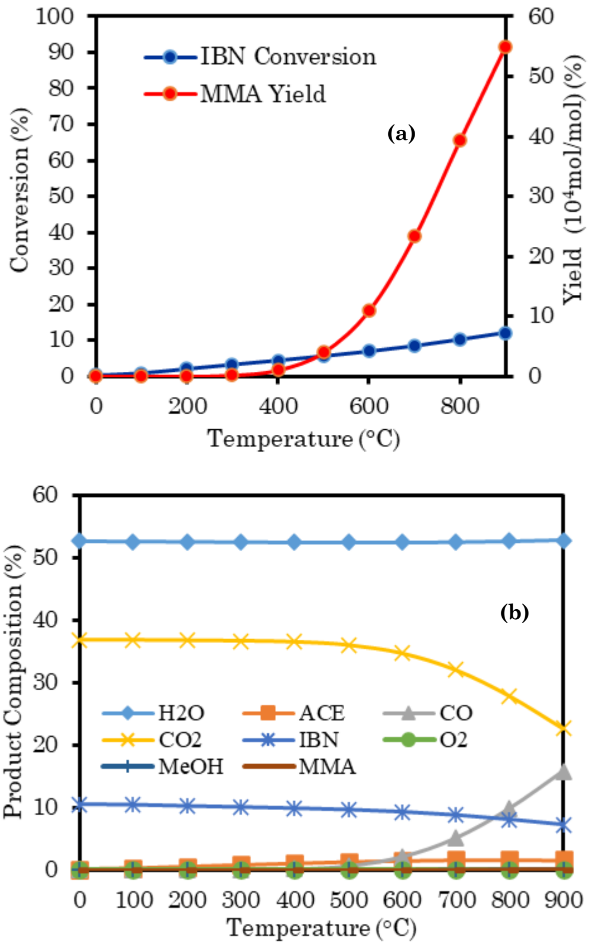


Figure 7. (a) The reaction profile of the temperature effect towards the conversion of IBN and MMA yield (based on Equation (4)); (b) The equilibrium product compositions as a function of temperature for MMA production.

With the conducted equilibrium product composition of R6' (Figure 7(b)), it revealed that the by-products such as CO_2, CO, and H_2O have dominated the production of MMA. Meanwhile, it can be seen that IBN occupied around a quarter of the product equilibrium composition because it remained unreacted, causing low conversion to desired product, MMA as shown in Figure 7(b). Therefore, the equilibrium composition of the reactants in the form of numerical data are tabulated in Table E8 of ESI for better visualization. It is found out that O_2 went to depletion, in other word, fully utilized or converted over the temperature range. While for IBN and MeOH, their compositions only varied slightly where equilibrium compositions of IBN decreased and MeOH increased when the temperature increases. Hence, it is believed that the low conversion is due to the absence of O_2, causing the IBN is unable to carry out further reaction. In order to confirm this finding, a feed ratio of reactants (IBN: O_2: MeOH) of 1:7:1 was applied in the simulation to investigate behaviour of the IBN in the excess O_2.

Figure 8 displays the simulation result of the MMA production route from IBN (based on R6' or Equation (4)) that carried out with the feedstock ratio of 1:7:1 under 1 bar. The high conversion of IBN was achieved, exceeding 90% over the temperature range. IBN even reached

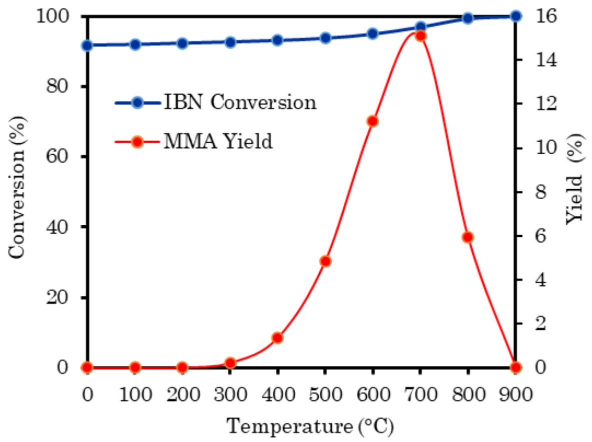


Figure 8. The reaction profile of the IBN conversion and MMA yield after adding by-products as a function of temperature (feedstock ratio of 1:7:1).

full conversion when the reaction temperature reached 800 °C and this has proven that IBN is ideally to be conducted under oxygen-rich conditions. Hence, this result confirmed the feasibility of setting the reactant's feed ratio at 1:7:1. On the other hand, the feedstock ratio of 1:7:1 achieved the highest rate of MMA production (15%) when the reaction temperature reached 700 °C. Generally, it remained unchanged at 0% from 0 to 300 °C and grew strikingly until reaching the peak (15%) at 700 °C, followed by reduction drastically to 0% with temperature increased afterwards. This indicates that decomposition of MMA occurred when the reaction temperature surpassed 700 °C.

To prove the low yield of MMA caused by its decomposition after 700 °C, the equilibrium compositions are evaluated and presented in Figure 9(a). It can be clearly seen that H_2O, CO_2, and CO existed as the dominant components in this MMA production route from IBN. H_2O and CO_2 occupied high composition, which mounted up to nearly 100% until 500 °C. Beyond 500 °C, H_2O remained constant at 55% while CO_2 decreased exponentially from 45 to 36% when the temperature rose from 500 to 900 °C. Upon investigation, it is found out that this MMA production route from IBN took over by a side reaction, which is the reaction of CH_3OH with the presence of O_2 and heat. The stoichiometry equation of this side reaction is shown in Equation (13). As a result, this side reaction produced CO_2 and H_2O, causing these two components to dominate the product distribution curve as shown in Figure 9(a). As evidence, enthalpy, entropy, and Gibbs free energy of formation and equilibrium constant for this side reaction are displayed in Table E9 and Figure 9(b) in order to have a better comparison with the single-step MMA production route from IBN. The results revealed that this side reaction has lowered enthalpy and Gibbs free energy of reaction as well as larger equilibrium constant value throughout the temperature range when compared to the main reaction, which is oxidative esterification of IBN to MMA (R6).

$$\text{Side reaction}: 1.5O_2 + CH_3OH \rightarrow 2H_2O + CO_2 \qquad (13)$$

Besides, it is noticeable that CO will only be formed after decomposition of CO_2 at 500 °C, and its composition rose steadily with the increasing temperature. Moreover, all reactants are found to be fully utilized with the low equilibrium compositions presented in Figure 9(b).

According to the temperature screening, the IBN conversion was 90% and above, whilst the MMA yield was 15%. Despite the current MMA yield being comparatively low and the temperature (approx. 700 °C) is high, this reaction route could be an emerging technology by saving the use of chemicals by implementing a shorter pathway. Withal, a shorter route could prevent the loss of intermediates conversion found in the multiple reaction routes. These might be an acceptable trade-off for the multi-stage reaction pathways. Several studies have adopted the one-step synthesis concept, whereby it has discussed that the selectivity of MMA could be well maintained at above 90% in the presence of Zn^{2+}/Al^{3+} in one-step oxidative esterification from MAL to MMA [27]. Another research has also put forward that fine-tuning of the catalyst's acid and base ratios could promote itaconic acid-to-MMA (38.2% selectivity)

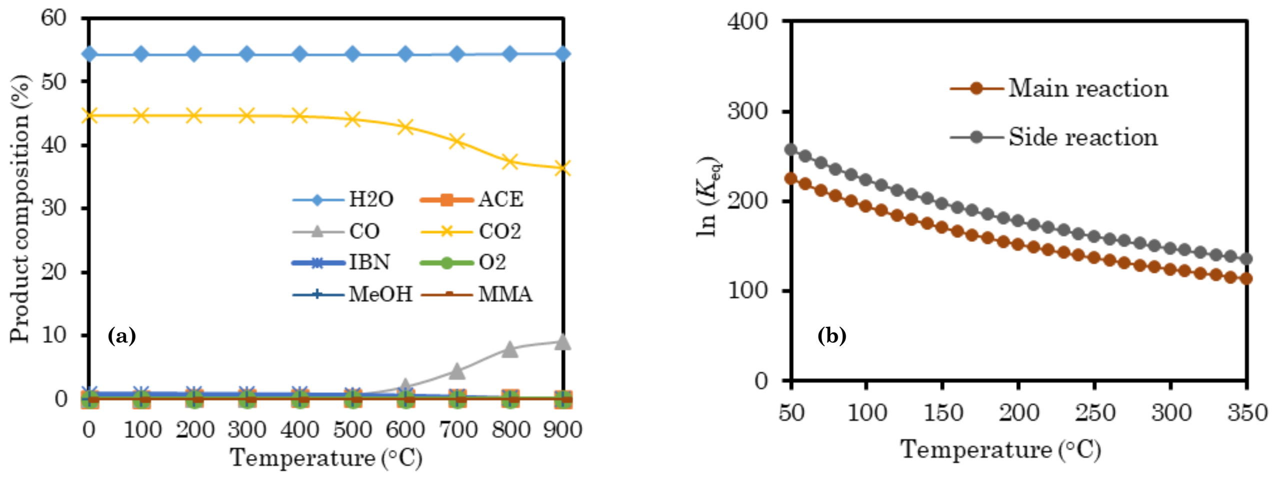


Figure 9. (a) The equilibrium product composition of IBN, MMA and by-products as a function of temperature for MMA production (feedstock ratio of 1:7:1); (b) The equilibrium constant as a function of temperature for side reaction and main reaction (R6).

in one-step decarboxylation-esterification [33]. Yet, no report on the one-step IBN conversion to MMA. Most of the oxygen-bearing feedstocks could initiate the reaction at lower energy compared to isobutene (hydrocarbon). Though higher energy is needed to induce oxidation-esterification of isobutene-to-MMA in the one-step process, the shorter pathways might offset the use of chemicals. Comparisons of MAA production with respect to feedstocks and reaction conditions are tabulated in Table 2.

3.2.2 Effect of pressure

To investigate the effect of pressure towards the designed MMA production route from IBN, the temperature set for the simulation was at 700 °C as MMA has the highest yield (15%) and reasonable conversion (97%). Certainly, the reactants, which are IBN, O_2, and MeOH, were fed at the ratio of 1:7:1. The result revealed that pressure has a negligible effect on the MMA production from IBN in a single step. This finding is supported by research reporting that the pressure effect is insensitive to the production of MMA from oxidation and esterification of MAL [13], which also in agreement with the literature [28]. Guan *et al.* [13] stated that the pressure can be neglected in the oxidative esterification of MAL and aldol condensation of MeOAc. The other report also showed the pressure has negative influence to the reaction system of dehydrogenation and partial oxidation of methanol to form formaldehyde intermediate [28]. Our study also gave the same result. It might due to the reactants conversion is constant with the pressure at a given temperature, whereby the oxidative esterification of isobutene to MMA is counteracted by the reaction of MMA with H_2O, and equilibrium constant is achieved. The result profile of the pressure screening is shown in Figure E1 of ESI.

3.2.3 Effect of feed compositions

In order to analyze the effect of feed composition of reactants which are IBN, O_2, and MeOH on the production of MMA that synthesized from IBN in a single step, different feedstock ratios were input and the result in terms of IBN conversion and MMA yield are tabulated in Table 3. The feedstock ratio of 1:7:1 was set as the reference point and optimum reaction temperature and pressure were identified to be 700 °C and 1 bar, respectively.

The full conversion of IBN (100%) has been achieved when the feedstock ratio was set to be 1:9:1 (Table 3). However, there is no MMA is

Table 2. Comparisons of MAA yield with respect to feedstocks and reaction conditions.

Feedstocks	Condition			Catalysts	Conversion (%)	MMA Yield[a] or Selectivity[b] (%)	Ref.
	Temp. (°C)	Molar Ratio of feedstock: methanol	Pressure (bar)				
Itaconic acid	250	-	12	Pt/Al_2O_3	100	84[a]; 38.2[b]	[33]
MAL	80	1:23	3	Zn-Al-Mixed Oxides Supported Gold	84.9	95.1[b]	[27]
MAA	100	1:1.5	-	SO_4^{2-}/TiO_2-SiO_2	-	80[a]	[34]
MAA	95.15	1:1.2	3	NKC-9 resin	80	-	[35]
methyl isobutyrate	400	1:0.5	-	Iron phosphate	55	40[a]; 73[b]	[36]
MAL	70	1:40	1	Gold/hydroxyapatite	100	99[b]	[22]
Methyl Propionate; Formaldehyde	320	1:1:1.5	1	Zr-Fe-Cs/SBA-15	26	93.6[b]	[37]
MAL	80	1:20	3	Pd–Pb/MgO–SBA-15	67.9	71.7[b]	[38]

Table 3. Effect of different feedstock ratio on single step MMA production from IBN.

Feedstock ratio (IBN:O_2:MeOH)	Conversion of IBN (%)	Yield of MMA (%)
1:7:1	96.95	15.10
1:9:1	100.00	0
1:3.5:1	43.11	22.15
1:2:1	17.49	24.77
1:2:3	29.29	24.74
1:2:0.5	29.07	24.70
2:2:1	10.90	21.19
0.5:2:1	28.68	24.62

being produced, resulting in 0% of MMA yield. The reason for zero yield is due to full domination of the side reaction, which is the reaction of MeOH with O_2. This side reaction, which is proven to be more thermodynamically favourable, whereby fully utilize the composition of O_2 to produce H_2O and CO_2. This leads to insufficient O_2 to react with IBN to give MMA. Next, reasonable high IBN conversion (97%) was achieved with 15% of MMA yield by reducing the feedstock ratio to 1:7:1, which was used in the simulation of temperature screening. It is observed that when reducing the composition of O_2 in the feedstock ratio, the IBN conversion decreased and MMA yield increased. To prove this, feedstock ratios of 1:3.5:1 and 1:2:1 with decreased O_2 composition were simulated. As a result, IBN conversion decreased drastically while MMA yield increased after reducing O_2 composition. IBN conversion dropped from 96.95 to 43.11% and 17.49% and MMA yield rose from 15.10 to 22.15% and 24.77% when feedstock ratios were set at 1:3.5:1 and 1:2:1, respectively. Therefore, the feedstock ratio of 1:2:1 is preferable as shown the highest MMA yield.

In addition, the influence of MeOH composition was studied by modifying the composition in feedstock ratio, at the same time, the composition of IBN and O_2 were kept constant. From the result shown in Table 1, MMA yield rarely deviates from each other, resulting in an average value of 24.74% when the compositions of MeOH were tuned. However, by comparison, the feedstock ratio of 1:2:1 still remained as the optimum feedstock ratio as it resulted in a slightly higher MMA yield which is 24.77%. Moreover, the composition of IBN in the feedstock ratio of 1:2:1 was also tuned to study the influence on MMA yield and IBN conversion. As a result, both feedstock ratios of 2:2:1 and 0.5:2:1 resulted in lower MMA yields, which were 21.19% and 24.62%, respectively. Succinctly, the highest MMA yield was achieved with feedstock ratio 1:2:1.

4. Conclusions

A shorter pathway, *viz.* one-step conversion of isobutene to methyl methacrylate, via a direct oxidative esterification process has been simulated. Thermodynamic analysis via Gibbs free energy minimization method demonstrated the feasibility of this route via the equilibrium constant. Temperature, pressure, and feedstock ratio screenings were also computed to give an optimum reacting environment. As a result, the designed route showed feasibility based on the equilibrium constant. The conversion of isobutene was 90% and along with 15% yield of methyl methacrylate at 700˚C and molar ratio isobutene: oxygen: methanol of 1:7:1. To achieve a higher yield of methyl methacrylate, the feedstock ratio was tuned to 1:2:1, the methyl methacrylate yield increased to approximately 25%. The main limitation of this reaction is the high temperature and occurrence of the side reaction of oxygen and methanol. Using catalysis with oxidative-esterification on light hydrocarbons is crucial to lowering the reaction temperature while suppressing the side production from methanol and oxygen. Mixed metal oxides and Keggin-type polyoxometalate will be the promising catalysts owing to its multi-metallic active sites and Lewis and Brönsted acidic sites. Moreover, hydrocarbon, like isobutene, is not costly as it is the byproduct of the petroleum refinery process; thus, the continuous supply of this feedstock to give MMA can divert the lab-scale production to an industrial scale. The one-step pathway is believed to be a potential emerging technology driven by saving chemicals and preventing the loss of intermediates during synthetic processes.

Acknowledgments

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ELECTRONIC SUPPORTING INFORMATION (ESI)

All individual stoichiometry Equations (E1 – E8) present in Figure 2 are stated as assigned to electronic supporting information (ESI).

Oxidation of IBN to produce MAL, [R1]:

$$C_4H_8 + O_2 \rightarrow C_4H_6O + H_2O \quad \text{(E1)}$$

Oxidation of MAL to produce MAA, [R2]:

$$C_4H_6O + 1/2\ O_2 \rightarrow C_4H_6O_2 \quad \text{(E2)}$$

Esterification of MAA with methanol to produce MMA, [R3]:

$$C_4H_6O_2 + CH_3OH \rightarrow C_5H_8O_2 + H_2O \quad \text{(E3)}$$

Oxidative esterification of MAL with oxygen and methanol to produce MMA, [R4]:

$$C_4H_6O + 1/2\ O_2 + CH_3OH \rightarrow C_5H_8O_2 + H_2O \quad \text{(E4)}$$

Oxidation of IBN to form MAA, [R5]:

$$C_4H_8 + 1/2\ O_2 \rightarrow C_4H_6O_2 + H_2O \quad \text{(E5)}$$

Oxidative esterification of IBN with oxygen and methanol to produce MMA, [R6]:

$$C_4H_8 + 3/2\ O_2 + CH_3OH \rightarrow C_5H_8O_2 + 2\ H_2O \quad \text{(E6)}$$

Oxidation of methanol to produce MAL, [R7]:

$$4\ CH_3OH + O_2 \rightarrow C_4H_6O + 5\ H_2O \quad \text{(E7)}$$

Dehydrogenation of methanol to produce formaldehyde, [R8]:

$$CH_3OH \rightarrow CH_2O + H_2 \quad \text{(E8)}$$

Table E1. Values of $G^\circ_{f@298K}$, $S^\circ_{f@298K}$ and $H^\circ_{f@298K}$ for different components recorded in Chemical Properties Handbook [11].

Component	$G^\circ_{f@298K}$ (kJ/mol)	$S^\circ_{f@298K}$ (kJ/mol.K)	$H^\circ_{f@298K}$ (kJ/mol)
H_2	0.000	0.000	0.000
H_2O	−228.600	−44.270	−241.800
O_2	0.000	0.000	0.000
CH_2O	−109.910	−20.0910	−115.900
CH_3OH	−162.510	−129.666	−201.170
C_4H_8	58.070	−251.451	−16.900
C_4H_6O	−57.600	−182.458	−112.000
$C_4H_6O_2$	−287.720	−269.059	−367.940
$C_5H_8O_2$	−241.590	−354.754	−347.360

Table E2. Heat capacities (C_p) for different components recorded in Chemical Properties Handbook [11].

Component	Temperature (K)	Coefficients for C_p equation (J/mol.K)				
		A	B	C	D	E
H_2	250 - 1500	25.399	2.0178E-02	-3.8549E-05	3.1880E-08	-8.7585E-12
H_2O	100 - 1500	33.933	-8.4186E-03	2.9906E-05	-1.7825E-08	3.6934E-12
O_2	50 - 1500	29.526	-8.8999E-03	3.8083E-05	-3.2629E-08	8.8607E-12
CH_2O	50 - 1500	34.428	-2.9779E-02	1.5104E-04	-1.2733E-07	3.3887E-11
CH_3OH	100 - 1500	40.046	-3.8287E-02	2.4529E-04	-2.1679E-07	5.9909E-11
C_4H_8	200 - 1500	32.918	1.8546E-01	7.7876E-05	-1.4645E-07	4.6867E-11
C_4H_6O	298 - 1200	14.506	1.5922E-01	3.1118E-04	-4.2100E-07	1.4222E-10
$C_4H_6O_2$	298 - 1200	-28.131	5.4744E-01	-5.3877E-04	2.8583E-07	-6.0864E-11
$C_5H_8O_2$	298 - 1500	-25.526	6.0628E-01	-5.0627E-04	2.2388E-07	-4.2286E-11

Table E3. Calculated enthalpy, entropy and Gibbs free energy of reaction for R1 – R8.

	$\Delta_r H°_{f@298K}$ (kJ/mol)	$\Delta_r S°_{f@298K}$ (kJ/mol.K)	$\Delta_r G°_{f@298K}$ (kJ/mol)
R1	-336.90	24.72	-344.27
R2	-255.94	-86.60	-230.12
R3	-20.05	-0.30	-19.96
R4	-275.99	-86.90	-250.08
R5	-351.04	-17.61	-345.79
R6	-612.89	-62.18	-594.352
R7	-516.32	114.86	-550.56
R8	85.27	109.58	52.60

Table E4. Conditions of Gibbs free energy of reactions.

$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$
-	+	Spontaneous at all temperature
+	+	Spontaneous only at high temperature
-	-	Spontaneous only at low temperature
+	-	Non-spontaneous at all temperature

Table E5. Calculated enthalpy, entropy and Gibbs free energy of reaction for A1 – A3.

	$\Delta_r H°_{f@298K}$ (kJ/mol)	$\Delta_r S°_{f@298K}$ (kJ/mol.K)	$\Delta_r G°_{f@298K}$ (kJ/mol)
A1	-461.08	110.15	-493.92
A2	-717.02	23.55	-724.04
A3	-737.07	23.25	-744.00

Table E6. Calculated enthalpy, entropy and Gibbs free energy of reaction for B1 – B3.

	$\Delta_r H°_{f@298K}$ (kJ/mol)	$\Delta_r S°_{f@298K}$ (kJ/mol.K)	$\Delta_r G°_{f@298K}$ (kJ/mol)
B1	-269.79	181.02	-323.76
B2	-525.73	94.42	-553.88
B3	-545.78	94.12	-573.84

Table E7. Calculated thermodynamic data for IBN, IBAN and TBA route.

	$\Delta_r H°_{f@298K}$ (kJ/mol)	$\Delta_r S°_{f@298K}$ (kJ/mol.K)	$\Delta_r G°_{f@298K}$ (kJ/mol)
IBN route	-612.89	-62.18	-594.35
IBAN route	-737.07	23.25	-744.00
TBA route	-545.78	94.12	-573.84

Table E8. Equilibrium composition data of IBN, O_2 and MeOH.

Temperature (˚C)	IBN	O_2	MeOH
0	24.9446	0.0000	$9.1518\text{x}10^{-10}$
100	24.7993	0.0000	$6.7900\text{x}10^{-7}$
200	24.5408	0.0000	$2.6712\text{x}10^{-5}$
300	24.2820	0.0000	0.0002594
400	24.0105	0.0000	0.001273
500	23.6806	0.0000	0.004142
600	23.2127	0.0000	0.01021
700	22.5187	0.0000	0.02082
800	21.5887	0.0000	0.03703
900	20.5399	0.0000	0.05956

Table E9. Thermodynamic data of the main reaction and side reaction.

	$\Delta_r H°_{f@298K}$ (kJ/mol)	$\Delta_r S°_{f@298K}$ (kJ/mol.K)	$\Delta_r G°_{f@298K}$ (kJ/mol)
Combustion of isobutene (side reaction)	-675.94	44.04	-721.914
R6: Oxidative esterification of IBN (main reaction)	-612.89	-62.18	-594.352

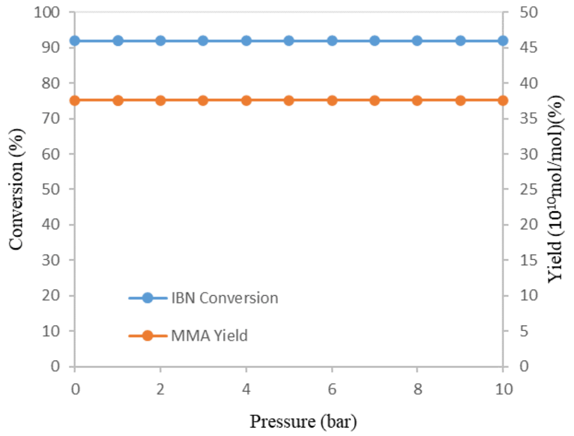

Figure E1. The reaction profile of the pressure effect towards the conversion of IBN and yield of MMA with by-products.

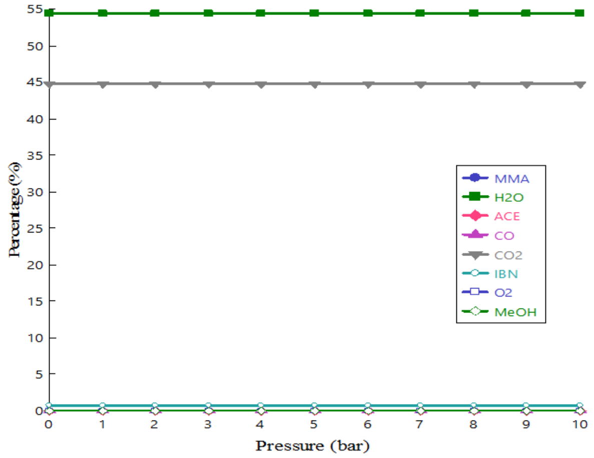

Figure E2. Equilibrium product composition of single step MMA production of MMA over different pressure.

As illustrated in Figure E1, conversion of IBN and MMA yield remained altered at 91.9% and 37.6%, respectively. This result revealed that pressure has negligible effect on the MMA production from IBN in single step. This finding is supported by the research carried by Guan *et al.* [13], reporting that pressure effect is insensitive to the production of MMA from oxidation and esterification of MAL. Besides, they also reported that reaction pressure can be neglected in the simulation of MMA production from methyl acetate (MeOAc) via aldol condensation and hydrogenation. However, equilibrium product composition of this single step MMA production route from IBN was carried out to further confirm its influence on pressure. Figure E2 displays the equilibrium product composition profile over range of pressure (0 to 10 bar).

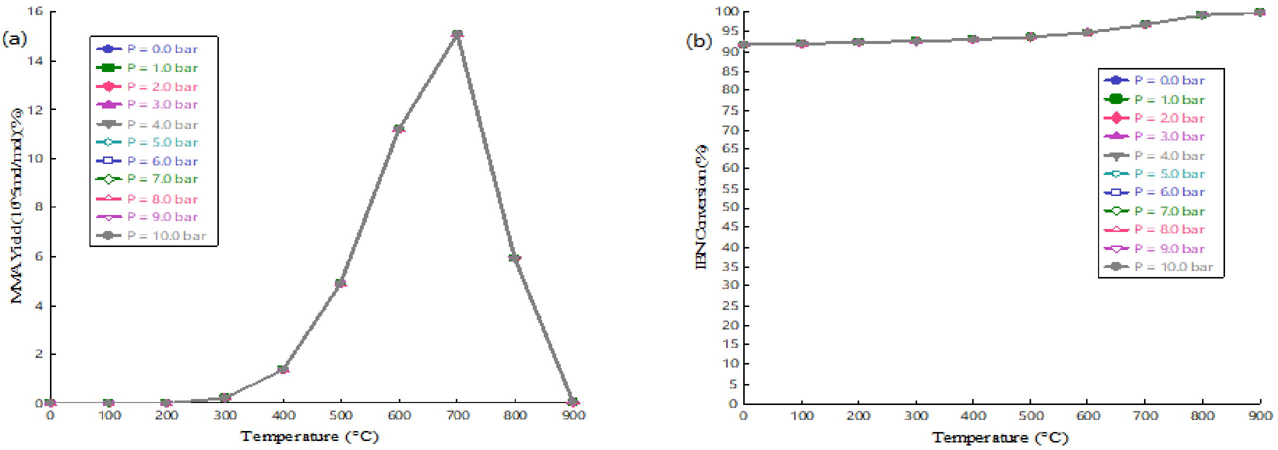

Figure E3. Overall influence of temperature and pressure on the (a) MMA yield and (b) IBN conversion on MMA production route from IBN (feedstock ratio of 1:7:1).

As pressure increase from 0 to 10 bar, it is hardly to observe any fluctuation on the components involved in this reaction which are MMA, H_2O, ACE, CO, CO_2, IBN, O_2 and MeOH. It is concluded that pressure effect is negligible in single step MMA production route from IBN. Thus, the optimum pressure is atmospheric pressure, which is much favorable in the aspect of economic and safety in the viewpoint of industrialization.