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

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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: O₂: MeOH ratio with 1:7:1. This route is mainly limited by the generation of side reactions from the reaction of CH₃OH and O₂. 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-
and North America, which has accounted for
this process is still applied by most MMA man-
years until 1982 [1]. Even until 21st century,
this process is still applied by most MMA man-
ufacturers, 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 concentrat-
ed H₂SO₄ to yield methacrylamide sulfate.
Then, methacrylamide sulfate was treated
with excess aqueous CH₃OH to form mixture of
MMA and ammonium bisulphate (NH₄HSO₄)
after hydrolyzation and esterification [2,12].
However, this conventional process has suf-
fered from two main drawbacks, which are
massive use of toxic reactants, HCN, and envi-
ronmentally detrimental co-production of
NH₄HSO₄[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 ex-
periments and research using C₂, C₃ and C₄ hy-
dercarbons as precursors have been widely de-
veloped to replace this conventional ACH pro-
cess [14–16].

Propylene, with the chemical formula of
C₃H₆, had derived acetone-cyanohydrin, which
was used as feedstock in the conventional ACH
process. Hence, the ACH process can be consid-
ered as a type of C₂-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 NH₄HSO₄ 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 atmos-
pheric 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 lim-
ited supply of propyne has restricted for com-
mercialization. Propyne which could be ob-
tained 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 C4-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 C4 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 (C4H8) 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, C4-based MMA production is a preferable route due to its environmental benignancy [9]. Hence, synthetic routes of MMA from C4 hydrocarbons have gained great interest and attention from researchers. Given the aspects from the economic and environment, IBN or TBA is favorable among C4 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 C4 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 C4 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-

![Reaction pathways from IBN to MMA](image)

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

<table>
<thead>
<tr>
<th>Routes</th>
<th>Descriptions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>MMA from ethylene is the condensation reaction of formaldehyde with propanol/propionaldehyde</td>
<td>[5,6]</td>
</tr>
<tr>
<td></td>
<td>MMA from ethylene via the intermediates such as propionaldehyde, MAL and MAA</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>LiIMA Process: Aldol condensation to give methacrolein (MAL), then the oxysterification of MAL with methanol to give MMA.</td>
<td>[2]</td>
</tr>
<tr>
<td>C3</td>
<td>Conventional ACH process</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>New ACH process uses propylene as the feedstock</td>
<td>[1,3]</td>
</tr>
<tr>
<td></td>
<td>The reaction of propyne and CO with Pd as the catalyst</td>
<td>[18]</td>
</tr>
<tr>
<td>C4</td>
<td>Isobutene oxidation to methacrylic acid (MAA)</td>
<td>[1,3]</td>
</tr>
<tr>
<td></td>
<td>Direct oxidation of isobutene to form MMA</td>
<td>[25,26]</td>
</tr>
<tr>
<td></td>
<td>Three-step process: isobutene-to-MAL; MAL-to-MAA; MAA-to-MMA</td>
<td>[1–3,9,23,24]</td>
</tr>
<tr>
<td></td>
<td>Two-step processes: isobutene-to-MAL; MAA-to-MMA or MAL-to-MAA; MAA-to-MMA</td>
<td>[1–3,9,23,24]</td>
</tr>
</tbody>
</table>
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 C₄ (oxidative esterification of methacrolein (MAL)) and C₃ (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/O₂ and MAL/methanol, whilst least effects from the temperature and pressure. The MMA production increases with the concentration of methanol and O₂ [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.](image-url)
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 H2O (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 H2O (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, H2O 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 H2O is produced as the by-product (R6). At the same time, two side reactions, which are oxidation of methanol to produce MAL and H2O (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 (\(G_f\)) 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)).

\[
G_f = \sum_{i=1}^{n} n_i \mu_i = \sum_{i=1}^{n} n_i \mu_i^0 + RT \sum_{i=1}^{n} n_i \ln \frac{f_i}{f_i^0} \tag{1}
\]

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

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

\[
f_i = \varphi_i \gamma_i P \tag{2}
\]

where \(\varphi_i\) is fugacity of component \(i\), \(\gamma_i\) 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:

\[
\mu_i + \sum_{j=0}^{k} \lambda_j a_{ij} = 0 \tag{3}
\]

where \(\lambda_i\) is Lagrange multiplier of component \(i\), and \(a_{ij}\) is number of atoms of element \(j\) in component \(i\).

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

\[
\sum_{i=1}^{n} n_i \left[ \mu_i^0 + RT \ln \frac{\varphi_i \gamma_i P}{f_i^0} + \sum_{j=0}^{k} \lambda_j a_{ij} \right] = 0 \tag{4}
\]

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 (\(G_{f}^{\varphi_{298K}}\)), Entropy of formation (\(S_{f}^{\varphi_{298K}}\)) and Enthalpy of formation (\(H_{f}^{\varphi_{298K}}\)) are also equated to zero for all components involved in the current study (H2, H2O, O2, CH2O, CH2OH, C2H4, C2H6O, C2H5OH, and C3H6O2) 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, \(\Delta G_{rxn}\), 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.
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, O₂, H₂, MeOH and FA, where MAL (R7) and FA (R8) are the by-products. The enthalpy of reaction (ΔHᵣᵣₑₐₓₚₚₑₓₚₑₚₑᵦₑₚₑₚₑₓₚₑₚₑₓₚₑₚₑₓₚₑₚₑₓₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚẹxₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑₓₑₚₑₚₑxlim; t = \frac{T(K)}{1000} \)
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 con-
stants for routes R1–R7 lie above the reference
line (\( \ln K_{eq} = 0 \)), indicating the feasibility of
these reaction routes. These reactions are fa-
vored 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 men-
tioned earlier. However, it gradually favors the
forward reaction when the temperature in-
creases. Figure 3 shows that R5–R7 have ex-
hibited 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 equa-
tions. Although R1, R2, and R4 have also exhib-
ited 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 thermody-
namically favorable route when compared to
the two- or three-step production pathways.
However, the side reaction - oxidation of meth-
anol to produce MAL (R7) has a significant ef-
fect 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 big-
ger when reaction temperature decreases.

These results also agrees well with the state-
ment above, where R7 displays less effect than
R6 at low reaction temperature.

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 in-
fluence on the production of MMA from MAA
as there is only slight deviation on the graph
throughout the experiment temperature dis-
played in Figure 3. Therefore, precise screen-
ing of the operating parameters, including re-
action temperature and feed composition, is
significant to investigate their influence on the
IBN-to-MMA production.

There are other C\(_4\) hydrocarbons, viz. isobu-
tane (IBAN) and tert-butanol (TBA), will sub-
stitute IBN in order to study their feasibilities
in the formation of MMA. Therefore, R1, R5 &
R6 with the involvement of IBN will be re-
placed with A1–A3 for isobutane (IBAN) route
and B1–B3 for the tert-butyl alcohol (TBA)
route.

![Figure 3. Equilibrium constant as a function of
temperature for Equation R1–R8.](image)

![Figure 4. (a) MMA production routes from
IBAN; (b) Equilibrium constant as a function of
temperature for the routes A1–A3.](image)
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 C₄ 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 4](image1.png)

![Figure 5](image2.png)

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 [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: O₂: MeOH) was input using stoichiometry ratio, 1:1.5:1, and the pressure was set at atmospheric pressure, 1 bar.

\[
C_8H_{18} + \frac{3}{2}O_2 + CH_3OH \rightarrow C_4H_8O_2 + 2H_2O \tag{10}
\]

\[
IBN\text{ conversion} = \frac{n_{IBN(\text{initial})} - n_{IBN(\text{final})}}{n_{IBN(\text{initial})}} \times 100\% \tag{11}
\]

\[
MMA\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\% \tag{12}
\]

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, O₂, MeOH, MMA, and H₂O, levelled out from 0 to 900 °C. The equilibrium composition of MMA and H₂O 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-
bon monoxide (CO), and carbon dioxide (CO₂), were taken into account, thus, the single-step MMA production route from IBN with by-products added (R₆') is shown as Equation (4):

\[
\text{R₆': } C₃H₆ + 4.5O₂ + 6CH₃OH \rightarrow C₅H₈O₂ + 9H₂O + C₃H₆O + CO₂ + CO
\]  

(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.

With the conducted equilibrium product composition of R₆' (Figure 7(b)), it revealed that the by-products such as CO₂, CO, and H₂O 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 O₂ 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 O₂, causing the IBN is unable to carry out further reaction. In order to confirm this finding, a feed ratio of reactants (IBN: O₂: MeOH) of 1:7:1 was applied in the simulation to investigate behaviour of the IBN in the excess O₂.

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 7](image-url)  
**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.

![Figure 8](image-url)  
**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 H₂O, CO₂, and CO existed as the dominant components in this MMA production route from IBN. H₂O and CO₂ occupied high composition, which mounted up to nearly 100% until 500 °C. Beyond 500 °C, H₂O remained constant at 55% while CO₂ 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 CH₃OH with the presence of O₂ and heat. The stoichiometry equation of this side reaction is shown in Equation (13). As a result, this side reaction produced CO₂ and H₂O, 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).

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

Besides, it is noticeable that CO will only be formed after decomposition of CO₂ 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](image-url)

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, O₂, 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 H₂O, 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, O₂, 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.

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.

<table>
<thead>
<tr>
<th>Feedstocks</th>
<th>Condition</th>
<th>Catalysts</th>
<th>Conversion (%)</th>
<th>MMA Yield or Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Itaconic acid</td>
<td>250°C</td>
<td>Pt/Al₂O₃</td>
<td>100</td>
<td>84[a]; 38.2[b]</td>
</tr>
<tr>
<td>MAL</td>
<td>80°C</td>
<td>Zn-Al-Mixed Oxides</td>
<td>84.9</td>
<td>95.1[b]</td>
</tr>
<tr>
<td>MAA</td>
<td>100°C</td>
<td>SO₂ₓ/TiO₂·SiO₂</td>
<td>-</td>
<td>80[a]</td>
</tr>
<tr>
<td>MAA</td>
<td>95.15°C</td>
<td>Supported Gold</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>methyl isobutyrate</td>
<td>400°C</td>
<td>Iron phosphate</td>
<td>55</td>
<td>40[a]; 73[b]</td>
</tr>
<tr>
<td>MAL</td>
<td>70°C</td>
<td>Gold/hydroxyapatite</td>
<td>100</td>
<td>99[b]</td>
</tr>
<tr>
<td>Methyl Propionate;</td>
<td>320°C</td>
<td>Zr-Fe-Cs/SBA-15</td>
<td>26</td>
<td>93.6[b]</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>80°C</td>
<td>Pd–Ph/MgO–SBA-15</td>
<td>67.9</td>
<td>71.7[b]</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Feedstock ratio (IBN:O₂:MeOH)</th>
<th>Conversion of IBN (%)</th>
<th>Yield of MMA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:7:1</td>
<td>96.95</td>
<td>15.10</td>
</tr>
<tr>
<td>1:9:1</td>
<td>100.00</td>
<td>0</td>
</tr>
<tr>
<td>1:3:5:1</td>
<td>43.11</td>
<td>22.15</td>
</tr>
<tr>
<td>1:2:1</td>
<td>17.49</td>
<td>24.77</td>
</tr>
<tr>
<td>1:2:3</td>
<td>29.29</td>
<td>24.74</td>
</tr>
<tr>
<td>1:2:0.5</td>
<td>29.07</td>
<td>24.70</td>
</tr>
<tr>
<td>2:2:1</td>
<td>10.90</td>
<td>21.19</td>
</tr>
<tr>
<td>0.5:2:1</td>
<td>28.68</td>
<td>24.62</td>
</tr>
</tbody>
</table>
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 O₂. This side reaction, which is proven to be more thermodynamically favourable, whereby fully utilize the composition of O₂ to produce H₂O and CO₂. This leads to insufficient O₂ 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 O₂ 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 O₂ composition were simulated. As a result, IBN conversion decreased drastically while MMA yield increased after reducing O₂ 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 O₂ 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. Sufficiently, 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 petrochemical 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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References


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]:
\[ \text{C}_6\text{H}_5 + \text{O}_2 \rightarrow \text{C}_6\text{H}_4\text{O} + \text{H}_2\text{O} \]  
(E1)

Oxidation of MAL to produce MAA, [R2]:
\[ \text{C}_6\text{H}_4\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_6\text{H}_6\text{O}_2 \]  
(E2)

Esterification of MAA with methanol to produce MMA, [R3]:
\[ \text{C}_6\text{H}_6\text{O}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}_6\text{H}_5\text{O}_2 + \text{H}_2\text{O} \]  
(E3)

Oxidative esterification of MAL with oxygen and methanol to produce MMA, [R4]:
\[ \text{C}_6\text{H}_5\text{O} + \frac{1}{2} \text{O}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}_6\text{H}_6\text{O}_2 + \text{H}_2\text{O} \]  
(E4)

Oxidation of IBN to form MAA, [R5]:
\[ \text{C}_6\text{H}_5 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_6\text{H}_6\text{O}_2 + \text{H}_2\text{O} \]  
(E5)

Oxidative esterification of IBN with oxygen and methanol to produce MMA, [R6]:
\[ \text{C}_6\text{H}_5 + \frac{3}{2} \text{O}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}_6\text{H}_6\text{O}_2 + 2 \text{H}_2\text{O} \]  
(E6)

Oxidation of methanol to produce MAL, [R7]:
\[ 4 \text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O} + 5 \text{H}_2\text{O} \]  
(E7)

Dehydrogenation of methanol to produce formaldehyde, [R8]:
\[ \text{CH}_3\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \]  
(E8)

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

<table>
<thead>
<tr>
<th>Component</th>
<th>$G^\circ_{\text{f}298\text{K}}$ (kJ/mol)</th>
<th>$S^\circ_{\text{f}298\text{K}}$ (kJ/mol.K)</th>
<th>$H^\circ_{\text{f}298\text{K}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>−228.600</td>
<td>−44.270</td>
<td>−241.800</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>CH(_2)(_2)O</td>
<td>−109.910</td>
<td>−20.091</td>
<td>−115.900</td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>−162.510</td>
<td>−129.666</td>
<td>−201.170</td>
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<tr>
<td>C(_6)H(_5)</td>
<td>58.070</td>
<td>−251.451</td>
<td>−16.900</td>
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<tr>
<td>C(_6)H(_6)O(_2)</td>
<td>−57.600</td>
<td>−182.458</td>
<td>−112.000</td>
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<tr>
<td>C(_6)H(_5)O(_2)</td>
<td>−287.720</td>
<td>−269.059</td>
<td>−367.940</td>
</tr>
<tr>
<td>C(_6)H(_5)O</td>
<td>−241.590</td>
<td>−354.754</td>
<td>−347.360</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Component</th>
<th>Temperature (K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>250 - 1500</td>
<td>25.399</td>
<td>2.0178E-02</td>
<td>-3.8549E-05</td>
<td>3.1880E-08</td>
<td>-8.7585E-12</td>
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<tr>
<td>H(_2)O</td>
<td>100 - 1500</td>
<td>33.933</td>
<td>-8.4186E-03</td>
<td>2.9906E-05</td>
<td>-1.7825E-08</td>
<td>3.6934E-12</td>
</tr>
<tr>
<td>O(_2)</td>
<td>50 - 1500</td>
<td>29.526</td>
<td>-8.8999E-03</td>
<td>3.8083E-05</td>
<td>-3.2629E-08</td>
<td>8.8070E-12</td>
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<tr>
<td>CH(_2)(_2)O</td>
<td>50 - 1500</td>
<td>34.428</td>
<td>-2.9779E-02</td>
<td>1.5104E-04</td>
<td>-1.2733E-07</td>
<td>3.3887E-11</td>
</tr>
<tr>
<td>CH(_2)OH</td>
<td>100 - 1500</td>
<td>40.046</td>
<td>-3.8287E-02</td>
<td>2.4529E-04</td>
<td>-2.1679E-07</td>
<td>5.9909E-11</td>
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<tr>
<td>C(_6)H(_5)</td>
<td>200 - 1500</td>
<td>32.918</td>
<td>1.8546E-01</td>
<td>7.7876E-05</td>
<td>-1.4645E-07</td>
<td>4.6867E-11</td>
</tr>
<tr>
<td>C(_6)H(_5)O(_2)</td>
<td>298 - 1200</td>
<td>-28.131</td>
<td>5.4744E-01</td>
<td>-5.3877E-04</td>
<td>2.8583E-07</td>
<td>-6.0864E-11</td>
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<tr>
<td>C(_6)H(_5)O</td>
<td>298 - 1500</td>
<td>-25.526</td>
<td>6.0628E-01</td>
<td>-5.0627E-04</td>
<td>2.2388E-07</td>
<td>-4.2286E-11</td>
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Table E3. Calculated enthalpy, entropy and Gibbs free energy of reaction for R1 – R8.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ_{298K}$ (kJ/mol)</th>
<th>$\Delta S^\circ_{298K}$ (kJ/mol.K)</th>
<th>$\Delta G^\circ_{298K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>-336.90</td>
<td>24.72</td>
<td>-344.27</td>
</tr>
<tr>
<td>R2</td>
<td>-255.94</td>
<td>-86.60</td>
<td>-230.12</td>
</tr>
<tr>
<td>R3</td>
<td>-20.05</td>
<td>0.30</td>
<td>-19.96</td>
</tr>
<tr>
<td>R4</td>
<td>-275.99</td>
<td>-86.90</td>
<td>-250.08</td>
</tr>
<tr>
<td>R5</td>
<td>-351.04</td>
<td>-17.61</td>
<td>-345.79</td>
</tr>
<tr>
<td>R6</td>
<td>-612.89</td>
<td>-62.18</td>
<td>-594.352</td>
</tr>
<tr>
<td>R7</td>
<td>-516.32</td>
<td>114.86</td>
<td>-550.56</td>
</tr>
<tr>
<td>R8</td>
<td>85.27</td>
<td>109.58</td>
<td>52.60</td>
</tr>
</tbody>
</table>

Table E4. Conditions of Gibbs free energy of reactions.

<table>
<thead>
<tr>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>Spontaneous at all temperature</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Spontaneous only at high temperature</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Spontaneous only at low temperature</td>
</tr>
<tr>
<td>+</td>
<td></td>
<td>Non-spontaneous at all temperature</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ_{298K}$ (kJ/mol)</th>
<th>$\Delta S^\circ_{298K}$ (kJ/mol.K)</th>
<th>$\Delta G^\circ_{298K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>-461.08</td>
<td>110.15</td>
<td>-493.92</td>
</tr>
<tr>
<td>A2</td>
<td>-717.02</td>
<td>23.55</td>
<td>-724.04</td>
</tr>
<tr>
<td>A3</td>
<td>-737.07</td>
<td>23.25</td>
<td>-744.00</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ_{298K}$ (kJ/mol)</th>
<th>$\Delta S^\circ_{298K}$ (kJ/mol.K)</th>
<th>$\Delta G^\circ_{298K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>-269.79</td>
<td>181.02</td>
<td>-323.76</td>
</tr>
<tr>
<td>B2</td>
<td>-525.73</td>
<td>94.42</td>
<td>-553.88</td>
</tr>
<tr>
<td>B3</td>
<td>-545.78</td>
<td>94.12</td>
<td>-573.84</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\circ_{298K}$ (kJ/mol)</th>
<th>$\Delta S^\circ_{298K}$ (kJ/mol.K)</th>
<th>$\Delta G^\circ_{298K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBN route</td>
<td>-612.89</td>
<td>-62.18</td>
<td>-594.352</td>
</tr>
<tr>
<td>IBAN route</td>
<td>-737.07</td>
<td>23.25</td>
<td>-744.00</td>
</tr>
<tr>
<td>TBA route</td>
<td>-545.78</td>
<td>94.12</td>
<td>-573.84</td>
</tr>
</tbody>
</table>

Table E8. Equilibrium composition data of IBN, O$_2$ and MeOH.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>IBN</th>
<th>O$_2$</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.9446</td>
<td>0.0000</td>
<td>9.1518x10$^{-10}$</td>
</tr>
<tr>
<td>100</td>
<td>24.7993</td>
<td>0.0000</td>
<td>6.790x10$^{-7}$</td>
</tr>
<tr>
<td>200</td>
<td>24.5408</td>
<td>0.0000</td>
<td>2.6712x10$^{-5}$</td>
</tr>
<tr>
<td>300</td>
<td>24.2820</td>
<td>0.0000</td>
<td>0.0002594</td>
</tr>
<tr>
<td>400</td>
<td>24.0105</td>
<td>0.0000</td>
<td>0.001273</td>
</tr>
<tr>
<td>500</td>
<td>23.6806</td>
<td>0.0000</td>
<td>0.004142</td>
</tr>
<tr>
<td>600</td>
<td>23.2127</td>
<td>0.0000</td>
<td>0.01021</td>
</tr>
<tr>
<td>700</td>
<td>22.5187</td>
<td>0.0000</td>
<td>0.02082</td>
</tr>
<tr>
<td>800</td>
<td>21.5887</td>
<td>0.0000</td>
<td>0.03703</td>
</tr>
<tr>
<td>900</td>
<td>20.5399</td>
<td>0.0000</td>
<td>0.05956</td>
</tr>
</tbody>
</table>

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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).

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^{\circ}_{298K}$ (kJ/mol)</th>
<th>$\Delta S^{\circ}_{298K}$ (kJ/mol.K)</th>
<th>$\Delta G^{\circ}_{298K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion of isobutene (side reaction)</td>
<td>-675.94</td>
<td>44.04</td>
<td>-721.914</td>
</tr>
<tr>
<td>R6: Oxidative esterification of IBN (main reaction)</td>
<td>-612.89</td>
<td>-62.18</td>
<td>-594.352</td>
</tr>
</tbody>
</table>

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).

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$_2$O, 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.