BIO/CATALYTIC SYNTHESIS OF METHACRYLIC ACID

by

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(Under the Direction of James Kastner)

ABSTRACT

Methacrylic acid was synthesized from the bio-based substrates citric acid, itaconic acid, and 2-hydroxyisobutyric acid. Hydrotalcite, a solid base catalyst, was employed to form methacrylic acid through decarboxylation of itaconic acid and citric acid. The effect of varying temperatures, catalyst mass, residence times and substrate concentrations on methacrylic acid concentration and yield was determined. Comparing yields of methacrylic acid in each series of reactions resulted in finding an optimum substrate to catalyst mass ratio where methacrylic acid yield reaches to its highest value (9.6 g-substrate/g-catalyst and 22.7% yield for citric acid, 6.4 g/g and 22.9% yield for itaconic acid). Catalyst reusability experiments resulted higher methacrylic acid yields. Methacrylic acid was also formed from 2-hydroxyisobutyric acid in a single-step dehydration reaction. Among these three substrates, the highest yield of methacrylic acid (71.48 %) was achieved at 275 °C and a 1 minute residence time using 2-hydroxyisobutyric acid and subcritical water.

INDEX WORDS: Methacrylic Acid, Base Catalysis, Decarboxylation, Bio-based

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CHAPTER 1

INTRODUCTION

In recent years, continued utilization of petroleum-based feedstocks in the chemical industry has become a growing global environmental and economic concern. Finding suitable bio-based and bio-renewable replacements for petroleum-based resources is one of the most important aims of the chemical industry. Production of polymers is a part of the chemical industry that usually involves petroleum-based synthesis routes. Petroleum-based polyesters, polyvinyl chloride (PVC) and polystyrene are well-known examples of polymers originating from petroleum resources. One effective step in approaching bio-based synthesis routes in polymer industry is using monomers that are obtained from bio-based feedstocks instead of petroleum-based resources. Ethylene (a monomer of polyethylene) produced from bioethanol (achieved via fermentation) is an example of using bio-based monomers in the polymer industry.

2-methylpropenoic acid, known more familiarly as methacrylic acid (MAA), is an organic acid with one carboxyl group as the main functional group. This organic acid is a significant monomer in the production of polymers, since it is used as a precursor for its esters like methyl methacrylate (MMA) and poly (methyl methacrylate) (PMMA). There are many industrial applications for methacrylic acid and methyl methacrylate as a result of excellent chemical resistance and the transparency of polymers synthesized from these two materials. Using these polymers as glass substitutes, cosmetic fillers, optical fibers and paint and adhesive additives is an example of some of important industrial applications of methacrylic acid and methyl methacrylate.

Industrially, methacrylic acid is produced using the hazardous acetone-cyanohydrin process. In the acetone-cyanohydrin process acetone and hydrogen cyanide are reacted with concentrated sulphuric acid resulting in methacrylamide acid sulphate. Further treatments with methanol, hydrolysis and esterification of the amide are necessary to produce a mixture of methacrylic acid and methyl methacrylate. The toxic starting materials, high process cost and bisulfate waste are severe problems rising from acetone-cyanohydrin process. Recently several research groups have reported the synthesis of MAA or MMA from bio-based substrates. Synthesis of methacrylic acid from 2-methyl-1,3-propanediol, which can be produced from the fermentation of glycerol, has been reported.[1]

Citric acid, itaconic acid, and 2-hydroxyisobutyric acid are important chemicals that can be obtained from biomass. These chemicals are non-toxic and readily biodegradable. One-step dehydration followed by a two-step decarboxylation of citric acid, one-step decarboxylation of itaconic acid, and one-step dehydration of 2-hydroxyisobutyric acid can form methacrylic acid. In a bio/catalytic approach, Le Nôtre et al. 2014 reported that methacrylic acid can be synthesized from fermentation derived itaconic acid and citric acid using solid transition-metal catalysts such as Pd/Carbon, Pt/Al_2O_3, and Ru/Carbon and homogeneous base catalysts such as sodium hydroxide.

Catalysis using a homogeneous base in chemical processes can cause severe problems such as corrosion of reactors, difficult separation and recycling of the catalyst and wastewater treatment. As a part of this work, methacrylic acid is synthesized using itaconic acid and citric acid in presence of hydrotalcite, a solid base catalyst. Hydrotalcite is a layered anionic clay with base sites originating from HCO_3^- on the surface. This solid-base catalyst can be employed in decarboxylation processes. Using hydrotalcite in decarboxylation of fatty acids is reported in literature. On the other hand, 2-hydroxyisobutyric acid is another potential bio-based substrate that can be converted to methacrylic acid by one-step dehydration. Subcritical water conditions are known for increased ion product at high temperatures. Due to an ion product effect, subcritical water conditions can act as acid/base catalysts. In this work, methacrylic acid was formed through dehydration of 2-hydroxyisobutyric acid under the subcritical water condition and was thus dehydrated using hydronium (resulted from ion product) as a catalyst.

CHAPTER 2

BACKGROUND AND LITERATURE ANALYSIS

2.1. Bio/Catalytic Approaches in Production of Methacrylic Acid

Methacrylic acid is used in production of plastics, moldings, fibers, resins and other organic compounds. The major product of methacrylic acid and methyl methacrylate is poly (methyl methacrylate), with an annual consumption of 2.1 million tons.[1] Currently, the hazardous acetone-cyanohydrin process is the main method for production of methacrylic acid. Toxic starting materials, high process cost and the large amount of bisulfate waste are severe problems from the acetone-cyanohydrin process. Another industrial method to produce methacrylic acid involves two oxidation steps. The first step is oxidation of isobutylene to methacrolein using mixed metal oxides of Mo and Fe, with promoters such as Co, Ni, and an alkali metal.[2] The second step involves oxidation of methacrolein to methacrylic acid that can take place over a phosphomolybidic catalyst containing Cu and V and alkali metal promoters. Other routes to methacrylic acid, based on C_2 compounds, have also been studied.[3] The processes based on C_2 carbonylation are implemented technologies in production of methacrylic acid and methyl methacrylate. Each of these processes involves propionate as an intermediate, which is condensed with formaldehyde to produce either methacrylic acid or a mixture of methacrylic acid and methyl methacrylate. Synthesis of methacrylic acid by vapor-phase aldol condensation of propionic acid with formaldehyde over silica-supported metal phosphate catalysts[4] and acid-base bifunctional catalysts such as MgO, SiO_2, Al_2O_3 and ZrO_2, with and without cesium[2] has also been reported.

In the last two decades, some research groups have reported bio/catalytic approaches in production of methacrylic acid. In 1994, Carlsson et al. studied sequential conversion of fermentation-derived citric acid to itaconic acid to methacrylic acid in near critical (220-370 °C) and supercritical water (375-400 °C).[5] At high temperatures, citric acid can decompose to products, which result from these molecule's functional groups: one hydroxyl and three carboxyl groups. These products can also be involved in some secondary reactions. Acids with a tertiary hydroxyl in α position can decompose to ketones in high temperatures.[6] Therefore, citric acid decomposes to acetone at elevated temperatures. *cis/trans*-Aconitic is an intermediate of citric acid at high temperatures. Citric acid forms *cis/trans*-aconitic with a dehydration step. Bruce et al. 1943 reported that aconitic acid decomposes to itaconic acid at temperatures higher than 180 °C. Itaconic acid can form methacrylic acid with one decarboxylation step. Itaconic acid equilibration in water solutions occurs very fast at high temperatures.[7] Hence itaconic acid may involve in a fast equilibrium with citraconic acid and mesaconic acid (itaconic isomers), faster than it decarboxylates to methacrylic acid. According to a study by Li et al. 2001 on the kinetics of reactions with no catalyst in reaction medium under near critical water conditions, the rate of itaconic acid isomerization is faster than decarboxylation.[7] Hence, mesaconic acid and citraconic acid are the results of itaconic acid isomerization. In the next step, itaconic acid and its isomers can decarboxylate to methacrylic acid. Itaconic acid can also form citramalic acid by adding water across its double bond. Figure 2.1 shows the suggested reaction pathways by Carlsson et al. 1994 for citric acid decomposition in hot liquid water.

Carlsson et al. 1994 performed experiments at temperatures ranging from 220 to 400 °C and at pressure of 34.5 MPa in plug flow reactors using sodium hydroxide as a homogeneous base catalyst. They reported that decarboxylation of itaconic acid to methacrylic acid is fast above 350 °C, although formation of byproducts such as acetic acid, pyruvic acid, acetone, and acetaldehyde and also methacrylic acid degradation products (since methacrylic acid is not stable in water at high temperatures) indicated a lower selectivity at these temperatures. Carlsson et al. 1994 reported slow decarboxylation of citric acid to itaconic acid with high selectivity at 250 °C and below. At all tested temperatures, independent of the substrate (itaconic acid or citric acid), almost identical byproducts were obtained. Results of studying the effect of itaconic acid residence time on methacrylic acid yield verified that methacrylic acid yield rises rapidly to almost a steady value. In a bio/catalytic approach synthesis of methacrylic acid by decarboxylation of itaconic acid and citric acid using solid-transition metal catalysts is also reported.[7] Transition metals with typical supports such as Pd/C, Ru/C, Pt/C and Pt/Al_2O_3 were tested for decarboxylation of itaconic acid and citric acid (in water) to methacrylic acid in batch reactors at temperatures of 200-250 °C and pressure of 1 bar argon. The highest methacrylic acid yields were achieved with Pd/C and Pt/C at 250 °C and 1 hour residence time (65%). Le Nôtre et al. 2014 reported that methacrylic acid could add water across its double bond, forming 2-hydroxyisobutyric acid. Degradation of 2-hydroxyisobutyric acid leads to the formation of pyruvic acid, acetone and other volatile compounds.[7]

In an enzymatic approach, acrylic acid and methacrylic acid are synthesized from enzymatic conversion of acrylonitrile and methacrylonitrile, respectively. ε-Caprolactam-induced *Rhodococcus rhodochocrous* J1 cells containing nitrilase are used for production of both acrylic acid and methacrylic acid.[8] Pyo et al. 2012 also reported production of methacrylic acid by two steps that involve an oxidation and a catalytic dehydration of 2-methyl-1,3-propanediol. Methacrylic acid is produced by a process involving bio-conversion of 2-methyl-1,3-propanediol to 3-hydroxy-2-methylpropionic acid *via* 3-hydroxy-2-methyl propanal and catalytic dehydration of the resulting acid. Cells of *Gluconobacter oxydans* grown on glycerol-based culture medium are used as the catalyst for bioconversion that involves alcohol dehydrogenase and aldehyde dehydrogenase enzymes. The product of bio-conversion is converted to methacrylic acid using titanium dioxide at 210 °C.

2.2. Solid-Base Catalysts

Base catalysts are particularly important in the areas of organic synthesis of fine chemicals. In base catalysis, a reaction is usually catalyzed by a hydroxide ion. There are many possible compounds that can act as sources for hydroxide ion such as sodium hydroxide. These sources of hydroxide ion can catalyze the chemical reactions homogeneously (liquid base catalysts). However, application of homogeneous acid and base catalysts in chemical processes results in severe problems such as corrosion of instruments, difficult separation and recycling of the catalyst and wastewater treatment. One effective step towards more environmental friendly processes is replacement of homogeneous catalytic systems by heterogeneous catalytic systems. There are two types of basic sites in solid-base catalysts: First, a Brønsted base site (a base accepts a proton from reactant) is one type of site and a second Lewis base site (a base donates an electron pair to the reactant) is possible. An example of Brønsted base catalysis is aldol condensation and Knoevenagel condensation where an H^+ is removed from a ketone with α-H to form anions.[9] The Tishchenko reaction with a basic site donating an electron pair to the carbonyl C atoms to form anions is an example for Lewis base catalysis. Table 2.1 is a list of different types of solid base catalysts gathered by Hattori et al. 2014. In solid base catalysts, basic sites are located on the surface. In order to activate these base sites, CO_2 and H_2O should be removed from the surface of base catalysts, therefore surface O atoms of metal oxides are exposed. To remove CO_2 and H_2O and have basic sites on surface, pretreatment at high temperatures is required.[9] The optimum pretreatment temperature depends on the type of reaction and the type of catalyst.

Hydrotalcite, alkaline earth metal oxides, supported alkali metal compounds, zeolites and clay minerals are examples of catalysts with basic sites on surface. Each of these catalysts can be used in a specific reaction. Isomerization, dehydration and condensation, alkylation and esterification are major reactions that occur in presence of base solid-base catalysts. Table 2.2 summarizes industrial applications of some of solid-base catalysts during years gathered by Hattori et al. 2014.

2.2.1. Effect of Reaction Medium Basicity on Catalytic Conversion of Itaconic Acid and Citric Acid to Methacrylic Acid

Basicity of the reaction medium plays an important role in catalytic synthesis of methacrylic acid from itaconic acid and citric acid.[5] The rate of decarboxylation of itaconic acid and citric acid to methacrylic acid is a function of the pH of the reaction media. A study by Li and Brill 2001 indicated that kinetics of itaconic acid degradation are highly dependent on the pH of the reaction medium. They have reported that in comparison to neutral, dianionated and protonated itaconic acid, the decarboxylation process occurs faster for itaconate monoanion and the decarboxylation rate is almost equal for both neutral itaconic acid and dianion itaconate.[10] Since decarboxylation of dianionated occurs slower than monoanionated itaconic acid, at higher pH lower yield and selectivity of methacrylic acid is expected.[5] On the other hand, at low pH methacrylic acid starts degrading by addition of water molecules to double bonds. Le Nôtre et al. 2014 reported an optimum amount of base in the reaction medium where methacrylic acid selectivity reaches to its highest value. Maximum methacrylic acid and minimum byproducts selectivity at 1 equivalent of sodium hydroxide was observed. Le Nôtre et al. 2014 achieved the same results with other types of base, which verifies that the effect of adding base is due to change of pH and not presence of ions.

2.3. Solid-Acid Catalysts

Like solid-base catalysts, solid acid catalysts have numerous applications in industry. Alkylation, esterification, amination, isomerization and cracking processes are examples of acid-catalyzed reactions.[11] The Nitto process for production of methylamine, BASF-process for t-butylamine production, Asahi-process for cyclohexanol production and production of thiocompounds are all applications of solid acid catalysts in industry. Solid-acid catalysts can have Brønsted (donates a proton to the reactant) and Lewis (accepts a pair of electron from reactant) acid sites on their surface. Silica-alumina is an example of a well-known solid-acid catalyst, which contains both Brønsted and Lewis acid sites. Application of solid acid catalysts in decarboxylation reactions has been reported. Wang et al. 2013 reported use of solid acid catalysts with Lewis acid sites such as gamma-Al_2O_3 (possessing Lewis acid sites) and SiO_2–Al_2O_3 (possessing both Brønsted and Lewis acid sites) in selective decarboxylation of gamma-valerolactone to 1-butene.[12]

2.3.1. Role of Solid-Acid Catalysts in Dehydration Processes

As it was mentioned in the previous section there are numerous applications of acid catalysts in industry. Recently, several studies indicate use of homogeneous and heterogeneous acid-catalyzed dehydration reactions. Use of phosphoric acid (homogeneous)[13] and sulfated zirconia (heterogeneous) [14] in dehydration of fructose to 5-hydroxyfurfural are examples of using both homogeneous and heterogeneous acid catalysts in dehydration reactions. Use of gamma-alumina in dehydration of methanol to dimethyl ether [15] as a solid acid catalyst has been reported. Strong Brønsted acid sites on silica-alumina have been also employed for dehydration of methanol and tert-butyl alcohol.[16]

2.4. Decarboxylation of Organic Acids

Decarboxylation is the removal of carbon dioxide from the carboxyl group of an organic compound. An organic chemical reaction usually requires one or more chemical steps to produce a specific compound. For example, citric acid requires one dehydration step, followed by two decarboxylation steps and itaconic acid only needs one decarboxylation step to produce methacrylic acid (Figure 2.1). Transition-metal catalysts such as platinum and palladium have been used in decarboxylation processes. Pt/C was used to decarboxylate fatty acids at 330 °C [17] and Pd/C was used in decarboxylation of alkyl carboxylic acids in water at 250 °C and 40-50 bar.[18] Pd catalysts have been also used in decarboxylation of glutamic acid and pyroglutamic acid to bio-based 2-pyrrolidone. Recently Le Nôtre et al. 2014 has reported the use of Pd/C and Pt/C in decarboxylation of citric acid and itaconic acid to methacrylic acid at 250 °C.

2.5. Hydrotalcite - An Acid-Base Bi-functional Catalyst

Hydrotalcite with the chemical formula of $Mg_4Al_2CO_3(OH)_{12} \cdot 4(H_2O)$ is known as a solid-base catalyst.[19] Hydrotalcite is a layered (brucite-like layers) anionic clay with base sites originating from HCO^-_3 on the surface.[20] Other than active base sites, Yamaguchi et al. 1999 reported the presence of acid sites on calcined hydrotalcite. Active acid-base sites are obtained through formation of Mg-O-Al bonds after calcination of hydrotalcite.[21] Yamaguchi et al. 1999 tested calcination temperatures ranging from 400-1000 °C and found that the most effective hydrotalcite for cycloaddition of carbon dioxide to epoxides was calcined at 400 °C.

Besides solid transition-metal catalysts, hydrotalcite can be employed in decarboxylation of fatty acids.[22] This solid base catalyst has been tested for decarboxylation of oleic acid with three different MgO contents. Higher MgO contents resulted in higher oleic acid conversion.

2.6. Dehydration and Decarboxylation in Subcritical Water

Water is a safe, readily available and environmentally friendly compound that can be used as a solvent and reaction media. Subcritical water is liquid water under pressure at temperatures between boiling point and critical temperature (critical point is at 374 °C and 22.064 MPa). The variation of water properties with increasing temperature in subcritical water has attracted much attention for catalysis in recent years. Water is a polar molecule at room temperature, which starts losing its polarity above the subcritical point so that water can act as an organic solvent at increased temperatures. Hence, the solubility of organic molecules in water increases in the subcritical water condition.[23]On the other hand, self-ionizing of water, known as ion product increases with increasing temperature of liquid water. This high acidity/basicity from the increased ion product makes hot liquid water a suitable media for acid/base-catalyzed reactions. Hot liquid water has also been employed in decarboxylation processes. Unsubstituted indoles have been produced by removal of 2-carboxyl groups using pyrolysis with derivatives of copper, in quinolone. However, by using hot liquid water, Indole-2-carboxylic acid is decarboxylated at 255 °C in water.[23] The resulted ester was hydrolyzed at 290 °C, and the product was decarboxylated to result in 69% yield of styrene.[23] Alkylation, condensation and isomerization are other examples of catalysis at hot liquid water.[24] Other than these reactions, some research groups have reported use of subcritical water in dehydration reactions. Ott et al. 2006 reported dehydration of glycerol to acrolein in subcritical water.[25] Dehydration of fructose to 5-hydroxymethyfurfural[26] and glucose to levulinic acid[27] at subcritical water condition has also been reported in literature.

2.7. Biological Routes in Synthesis of Substrates

There is a new interest in replacement of fossil-based resources with sustainable resources of energy and material. Fermentation medium are used in production of many biological compounds. Citric acid, itaconic acid and, 2-hydroxyisobutyric acid are the examples of organic materials that can be produced through fermentation processes. The methods for synthesis of these materials will be explained in the following sections.

2.7.1. Synthesis of Citric Acid

Citric acid, a tricarboxylic acid, is a readily available carboxylic acid mostly found in citrus fruits. This carboxylic acid is a metabolic intermediate of the TCA cycle that is also found in plants and animals. The main industrial route in production of citric acid is fermentation of sugar using *Aspergillus niger* on sugars. The yield of citric acid from this strains often reaches to 70% of the theoretical yield on carbon source.[28] In order to reach the maximum yields of citric acid cofactors such as Cu^{2+}, Fe^{2+}, Mg^{2+} and Mn^{2+} are used in the fermentation medium. The starting pH is usually around 5 and after nitrogen metabolism it drops to around 3. Separation of citric acid from fermentation medium starts with precipitation of oxalic acid and then the mycelium is filtered through centrifuges or rotating filters. Precipitation of citric acid occurs at almost a neutral pH at temperatures ranging from 70 to 90 °C. Then citric acid is recovered through filtering. Higher grades of citric acid can be obtained by dissolving with sulfuric acid or treating with charcoal.[29]

2.7.2. Synthesis of Itaconic Acid

Itaconic acid is a dicarboxylic acid that can form methacrylic acid with removal of one carbon dioxide molecule. Baup discovered itaconic acid in 1837 as a thermal decomposition product of citric acid.[30] Since the 1960s the production of itaconic acid is achieved by the fermentation of sugars in presence of *Aspergillus terreus*.[30] *A. terreus* is still the main production host for itaconic acid with concentrations of 80-86 g L^{-1}.[31] One of the well-known pathways in fermentation of itaconic acid is suggested by Bentley and Thiessen 1957.[32] This pathway involves glycolysis and the TCA cycle so that pyruvate is generated through glycolysis of glucose. Then the pathway is divided into two parts. The first part of the pathway involves metabolism of Acetyl-CoA resulting in release of carbon dioxide. In the other part, the carbon is converted to oxaloacetate using the released carbon dioxide from Acetyl-CoA metabolism. In the first steps of the TCA cycle, citrate and *cis*-aconitate are formed. Towards the end of the cycle, *cis*-aconitate decarboxylase forms itaconic acid releasing carbon dioxide.[32] This fermentation process usually occurs at around 40 °C in presence of adequate oxygen with glucose or sucrose as the fermentation substrate.[30] The regular separation methods are used in recovery of itaconic acid from fermentation medium. After removal of mycelium and solids (by filtration), evaporation at acidic conditions, cooling and crystallization are next steps in obtaining an industrial grade itaconic acid.[33]

2.7.3. Synthesis of 2-Hydroxyisobutyric Acid

2-Hydroxyisobutyric acid, a hydroxy monocarboxylic acid, is isobutyric acid with a hydroxyl group at position 2. This monocarboxylic acid is known as an intermediate of methyl *tertiary*-butyl ether (MTBE) biodegradation pathway. 2-hydroxyisobutyric acid can easily form methacrylic acid through one step dehydration (Figure 2.1). In recent years, biohydrolysis of acetone cyanohydrin, biooxidation of tert-butanol and bioisomerization of 3-hydroxyisobutyric acid are some biotechnological routes that have been proposed in the synthesis of 2-hydroxyisobutyric acid.[34] Among all these approaches, only bioisomerization of 3-hydroxyisobutyric acid employs a renewable carbon source. 3-hydroxyisobutyric can be produced from renewable substrates using microorganisms. In a recent study, a microbial fermentation using recombinant of *Cupriavedus necator* H 16 has been developed. It is known as a PHB-producing bacterium, using cobalamin-dependent mutase in synthesis of 2-hydroxyisobutyric acid.[35] In the process of producing PHB starting from sugar, two acetyl-CoA molecules are transformed to acetoacetyl-CoA using 3-ketothiolase then acetoacetyl-CoA is converted to (R)-3-hydroxybutyryl-CoA by acetoacetyl-CoA reductase in presence of NADPH and the last step would be using PHB synthase to polymerize (R)-3-hydroxybutyryl-CoA.[35] In order to produce 2-hydroxyisobutyric acid the last step must be blocked, therefore an engineered strain of *Cupriavedus necator* H 16 (deficient in PHB synthase gene) has been used. Therefore(R)-3-hydroxybutyryl-CoA can be converted to 2-hydroxyisobutyryl-CoA using cobalamin-dependent 2-hydroxyisobutyryl-CoA mutase. Finally 2-hydroxyisobutyric acid can be formed through hydrolysis of 2-hydroxyisobutyryl-CoA.[35]

2.8. Impact of Key Components in Fermentation Medium on Catalyst Activity

Residual components of fermentation media can have an impact on heterogeneous catalysis. Some studies indicate loss of activity for heterogeneous catalysts in presence of fermentation impurities. Miller et al. 2008 reported loss of activity for ruthenium in hydrogenation of fermentation-derived lactic acid due to the presence of amino acids and proteins in fermentation medium. In a study by Elliott et al. 2004 on hydrogenation of sugars, ammonium showed a significant inhibition effect on the Ru and Ni catalysts. Carbon catalysts, containing sulfonic acid, for the esterification of succinic acid also show loss of activity due to the adsorption of organic species on the catalyst.[36] As far as catalyst activity of metals is concerned, impurities in fermentation media that can cause problems are sulfate for metal sulfide formation, calcium, magnesium, phosphate and proteins for catalyst pore plugging, sulfate for metal sulfide formation on metal catalyst, sodium and potassium for alkali attack, urea for metal complex formation and chloride for reaction with metal catalysts. Sulfur is a known compound in poisoning of palladium catalysts.[37] Poisoning of the Pd catalyst is partly irreversible due to direct interactions between Pd and SO_2.[38] Hydrogen treatment of poisoned palladium catalysts (with sulfur) applied in selective hydrogenation of styrene to ethylbenzene was effective in partially elimination of the sulfur compound.[39]

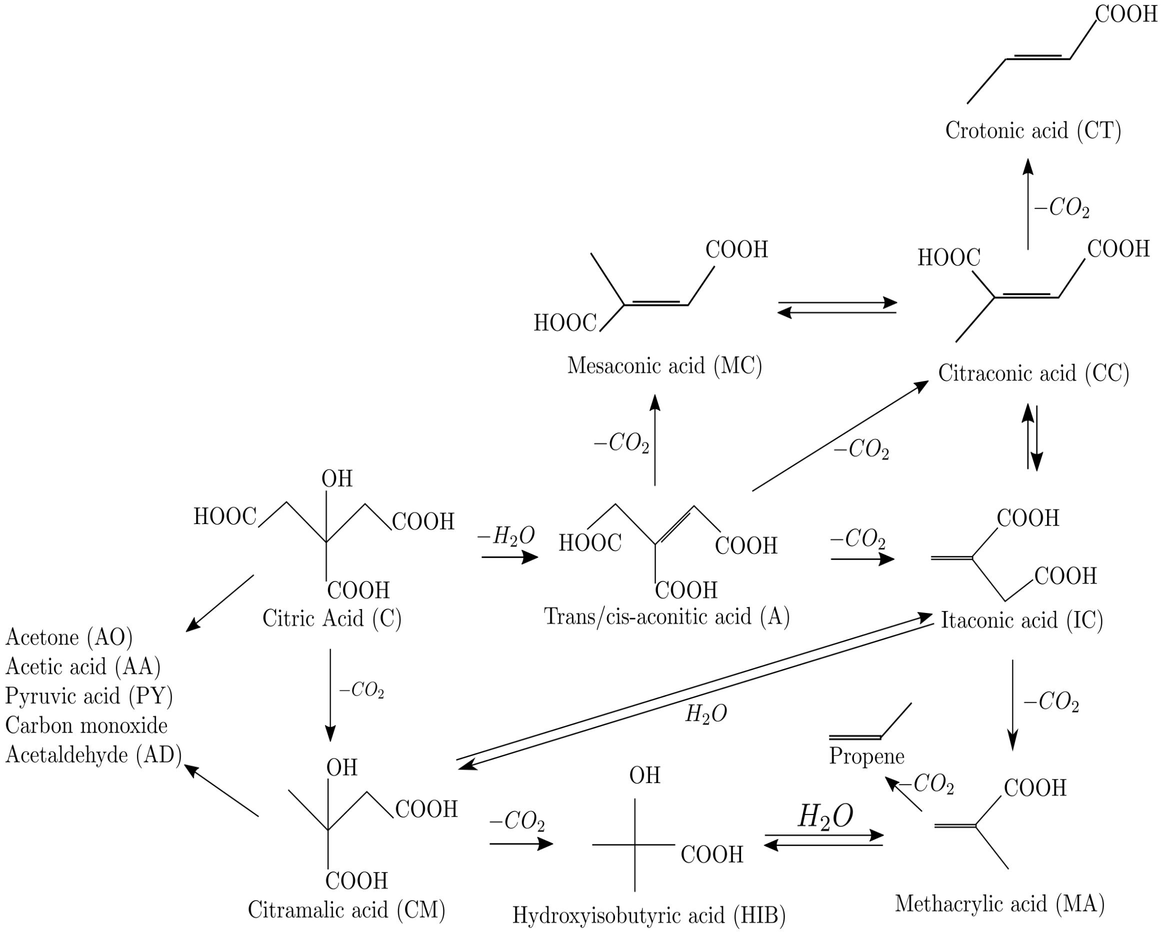


Figure 2.1: Important pathways for decomposition of citric acid in hot liquid water (obtained from Carlsson et al. 1994).[5]

Table 2.1: List of different solid base catalysts (obtained from Hattori et al. 2014 [9])

(1) Single Component metal oxides
- Alkaline earth metal oxides - Rare earth oxides - Other oxides: Al_2O_3, ZrO_2, Y_2O3, ZnO
(2) Double Components metal oxide
- ZnO- Al_2O_3, MgO-TiO_2
(3) Zeolites
- Alkali ion exchanged zeolites - Alkali ion-added zeolites
(4) Supported alkali metal compounds
- Alkali metal compounds on alumina - Alkali metal compound on silica - Alkali metal ions on alkaline earth oxides
(5) Clay minerals
- Hydrotalcite - Chrysolite - Sepiolite
(6) Non-oxides
- KF supported on alumina - Lanthanide imide and nitride on zeolite - Metal oxynitrides

Table 2.2: Industrial applications of solid base catalysts (From Hattori et al. 2014 [9])

Reaction	Catalyst	Year
Alkylation		
- Alkylation of phenol with methanol	- MgO	1985
- Alkylation of xylene with butadiene	- Na/K_2CO_3	1995
- Alkylation of cumene with ethylene	- Na/KOH/Al_2O_3	1988
Isomerization		
- Isomerization of safrole to isosafrole	- Na/NaOH/Al_2O_3	1988
- Isomerization of 2,3-dimethyl-1-butene	- Na/NaOH/Al_2O_3	1988
- Isomerization of 3,5-vinylbicycloheptane	- Na/NaOH/Al_2O_3	1988
- Isomerization of 1,2-propadiene	- K_2O/Al_2O_3	1996
Dehydration/Condensation		
- Dehydration of 1-cyclohexylethanol	- ZrO_2	1986
- Dehydration of propylamine-2-ol	- ZrO_2/KOH	1992
- Isobutyraldehyde to diisopropyl ketone	- ZrO_2	1973
- Isobutyraldehyde dehydrotrimerization	- BaO-CaO	1998
Esterification		
- Ethylene oxide esterification	- Hydrotalcite	1994
- Triglycerides transesterification	- ZnO-Al_2O_3	2006
Other		
- Carboxylic acids to aldehydes	- ZrO_2-Cr_2O_3	1988
- Thiols from alcohols with hydrogen sulfide	- Alkali/Al_2O_3	1988
- Cyclization of imine with sulfur dioxide	- Cs-zeolite	1995

CHAPTER 3

RATIONALE

Catalytic decarboxylation of itaconic acid and citric acid is a possible bio-based route in synthesis of methacrylic acid. Both itaconic acid and citric acid are substrates that can be generated from fermentation processes. Using these renewable and environmentally friendly substrates is definitely preferred over the hazardous acetone cyanohydrin process currently being used as the main industrial route in production of methacrylic acid. Literature review analysis indicates use of transition-metal catalysts such as palladium and platinum in synthesis of methacrylic acid from itaconic acid and citric acid. The importance of reaction medium basicity in decarboxylation of itaconic acid and citric acid to methacrylic acid was also discussed in the previous chapter. Homogeneous base catalysts like sodium hydroxide were used to achieve higher methacrylic acid selectivity in previous studies. However, corrosion of reactors, difficult separation and recycling of the catalyst, and wastewater treatment are drawbacks of using homogeneous base catalysts such as sodium hydroxide. In order to reduce these problems, heterogeneous base catalysts can be promising replacements for homogeneous base catalysts in industry.

One of the aims of this work was to determine the kinetics of methacrylic acid formation from citric acid and itaconic acid over a solid base catalyst such as hydrotalcite. Use of hydrotalcite in decarboxylation reactions is reported. Citric acid requires a one-step dehydration followed by a two-step decarboxylation and itaconic acid requires a one-step decarboxylation to form methacrylic acid. In the previous chapter, the effect of different calcination temperatures on hydrotalcite activity and active site exposures was also discussed. In this work, hydrotalcite calcined in varying temperatures has been tested to determine the effect of catalyst calcination temperature on methacrylic acid formation. Since transition-metal catalysts and homogeneous base catalysts were used simultaneously to achieve higher methacrylic acid yield and selectivity, in this work a solid base catalyst impregnated with a transition-metal catalyst is hypothesized to increase methacrylic yield and selectivity. On the other hand, solid acid catalysts such as gamma-Al_2O_3 and SiO_2–Al_2O_3 have been used in previous studies for decarboxylation purposes. Therefore, in this work gamma-Al_2O_3 and SiO_2–Al_2O_3 were applied in decarboxylation of citric acid and itaconic acid to methacrylic acid.

Other than citric acid and itaconic acid, 2-hydroxyisobutyric acid is another possible substrate- synthesized through biotechnological routes- for synthesis of methacrylic acid. 2-hydroxyisobutyric acid can form methacrylic acid through one step dehydration. In previous chapter it was discussed that solid acid catalysts are effective in numerous dehydration reactions. Yamaguchi et al. 1999 reported appearance of acid sites on hydrotalcite after calcination. Therefore, solid acid catalysts and hydrotalcite were applied in dehydration of 2-hydroxyisobutyric acid to methacrylic acid.

CHAPTER 4

EXPERIMENTAL METHOD

4.1. Materials

4.1.1. Starting Materials

Itaconic acid and citric acid monohydrate were purchased from Sigma-Aldrich and 2-hydroxyisobutyric acid (2HIB Acid) was purchased from TCI Co. Desired concentrations of each substrate was prepared using deionized water. Sodium hydroxide (Fisher Scientific), albumin, bovine (Sigma), D-(+)-glucose (Sigma), sodium phosphate dibasic heptahydrate (Sigma) and sodium sulphate (Sigma) were purchased in order to study the effect of fermentation medium on catalyst activity and methacrylic acid yield.

4.1.2. Catalyst Preparation

The raw hydrotalcite (HTC) powder with an MgO/Al_2O_3 ratio of 4.0-5.0 was purchased from Sigma-Aldrich. The HTC was calcined at 300 °C, 400 °C and 500 °C overnight and then allowed to cool. The powder was then stirred in DI water to make a paste, and the paste was placed in a 105°C drying oven overnight. Then the dried hydrotalcite was smashed and sieved to a particle size between 0.5 mm and 1 mm.

Literature review analysis indicates the use of transition-metal catalysts such as palladium and platinum in production of methacrylic acid from itaconic acid.[7] The importance of reaction medium basicity in decarboxylation of itaconic acid and citric acid to methacrylic acid was also discussed in the background and literature analysis chapter. Therefore, a solid-base catalyst impregnated with a transition metal was synthesized in this work. Palladium on HTC was prepared using incipient wetness impregnation.[40] Incipient wetness impregnation is a technique for the synthesis of heterogeneous catalysts. The active metal precursor is dissolved in aqueous solution. Then a volume of metal containing solution equal to the catalysts pore volume on a weight basis is added to the catalyst support. Capillary action draws the solution into the pores. In our case, a 5 wt. % palladium (II) nitrate dihydrate (40% Pd basis, Sigma-Aldrich) solution in deionized water was prepared. Nikolopoulos et al. 2005 used palladium chloride salt for impregnating hydrotalcite catalyst. Since chloride can have a poisoning effect in reaction medium, the nitrate salt was used. After adding the solution to the hydrotalcite powder-precalcined at 400 °C (containing the same pore volume as the volume of the solution that is added), the catalyst was dried at 120 °C for two hours, calcined at 400 °C for two hours and then crushed and sieved to the desired particle size. Prior to reaction the sample was reduced in a tubular reactor system at 450 °C for 8 hours in flowing 100 % hydrogen (Airgas).[40] Pd on activated carbon (5 wt. % -Alfa Aesar) was also reduced for 8 hours in flowing 100 % hydrogen (100 mL min^{-1}) at 450 °C.

Use of solid acid catalysts possessing Lewis acid sites in selective decarboxylation is reported in literature.[12] Gamma-Al_2O_3 possesses Lewis acid sites and SiO_2–Al_2O_3 possesses both Brønsted and Lewis acid sites. Gamma-Al_2O_3 (Strem Chemicals) and SiO_2–Al_2O_3 (Sigma-Aldrich) were calcined at 550 °C in air for four hours to produce acid sites.

Using iron containing catalysts in catalytic decarboxylation has been reported.[41] Zhang et al. 1999 reported catalytic decarboxylation of fatty acids by iron-containing minerals. Hence for the purpose of decarboxylation reaction, an iron oxide catalyst was prepared using deposition of nanoparticles on carbon with a supercritical water method by Xu et al.[42]A volume of 150 mL of $Fe(NO_3)_3.9H_2O$ (Sigma-Aldrich, ACS reagent of minimum purity 98 wt.%) solution (0.5 M) was made with deionized water. Then a 30.3 g amount of activated carbon (Sigma-Aldrich, Norit RO 0.8) pellets were added to the iron salt solution. The solution was subjected to sonication treatment for 45 minutes at room temperature. After five days of soaking, the mixture was divided into three batches (each 10.1 grams of activated carbon and 50 mL of the solution). Each batch was treated under helium gas (Airgas-UHP 300) in a high-pressure reactor system (PARR Instruments). Starting pressure was 750 psi to the final pressure of 4050 psi. Starting temperature was 17 °C and final temperature was 355 °C. The mixture was maintained at 355 °C for 90 minutes. Finally, the reactor was cooled down to 33 °C. The activated carbon pellets were separated from the mixture and washed several times with deionized water and dried overnight in the oven.[42]

4.2. Experimental Procedure

Production of methacrylic acid was performed in a 75 mL vessel (total volume) of a PARR 5000 Multiple Reactor System (with 6 vessels). The vessel was loaded with 40 mL of substrate solution in DI water, and catalyst was mixed using a magnetic stir bar inside the vessel. The vessel was sealed using the vessel cap with six screws. The mixture was stirred with a magnetic bar stirrer at 750 rpm. The headspace of the vessel was charged with 500 psi ultra high purity helium (Airgas-UHP 300) through a needle valve. Prior to pressurizing, the headspace was purged with helium for 1 minute to remove any impurities in headspace of the vessel. The vessel was heated using a heating well at an average heating rate of 9 °C /min. The stirrer bar is allowed to agitate during heat-up. The residence time was measured after reaching the desired temperature. The temperature was measured by a thermocouple in an alloy thermo well. Figure 4.1 shows a sample plot of temperature versus time during a reaction with 15 minutes residence time at 250 °C. The reaction pressure versus time plot (Figure 4.2) shows that the pressure rises from 34.5 bar (500 psi) to 59 bar (855 psi) at a temperature of 250 °C.

Once the reaction was completed, the vessel was cooled down using a water bath at room temperature. After taking gas sample (using 1 liter Tedlar bag), the headspace pressure is released through a second needle valve. The catalyst is removed from the liquid product using filter paper (Whatman, qualitative 11 μm pore size).

4.3. Calculations

4.3.1. Liquid Products

Methacrylic acid and by-product concentrations (grams per liter) were determined using High Performance Liquid Chromatography (HPLC). Considering that the volume of reaction is 40 mL, the moles of each compound are calculated through molar weight. In order to calculate yield and selectivity of each compound and conversion of reaction substrate the following equations were applied.

$$\%\,Yield\ of\ Compound\ i = \frac{Moles\ of\ Compound\ i\ Generated}{Moles\ of\ Substrate\ Charged} * 100 \qquad \text{Eq. (1)}$$

$$Conversion\ of\ Substrate\ (\mathrm{X}) = \frac{Moles\ of\ Substrate\ Reacted}{Moles\ of\ Substrate\ Charged} \qquad \text{Eq. (2)}$$

$$\%\ Selectivity\ of\ Methacrylic\ Acid = \frac{Moles\ of\ Methacrylic\ Acid\ Generated}{Moles\ of\ Substrate\ Converted} * 100 \quad \text{Eq. (3)}$$

4.3.2. Gas Products

Gas Chromatography –Thermal Conductivity Detection (GC-TC) was performed for gas analysis. Gas samples were taken after the reactor was cooled down at room temperature. A volume of 50 microliters of each gas sample was injected on GC-TCD. The percent CO_2 (by volume) of each sample was calculated using the peak area and standard curve of CO_2. In order to calculate the number of carbon dioxide moles, total moles of gas in the reactor was calculated using ideal gas law. The total moles of gas multiplied by percent CO_2 will result the number of CO_2 moles (n):

$$n_{CO2} = \frac{PV}{RT} * \%CO2 \qquad \text{Eq. (4)}$$

P= Reactor Pressure

V= Reactor Headspace Volume

R= Universal Gas Constant 8.314 J/K.mol

T= Temperature of The Gas after cool-down

4.4. Analysis of Liquid and Gas Products

Product concentrations (liquid sample) were determined using High Performance Liquid Chromatography (HPLC). HPLC (Shimadzu LC-20 AT) was performed by using an autosampler and pump with 7 mN H_2SO_4 eluent and 0.6 mL min^{-1} flow at 60°C. The sample injection volume and run time were 5 microliter and 30 minutes, respectively. A Coregal 64-H transgenomic column (7.8 x 300 mm) was used in this instrument. The methacrylic acid peak was verified with UV detection at 210 nm. Methacrylic acid was also verified with Gas Chromatography-Mass Spectrometry (GC-MS) using an Agilent GC-MSD. R- match (matching mass spectrum of compound to library) and probability algorithms were used to verify methacrylic acid. The identification of each compound was based on a search against a mass spectral database (NIST 2008 library). Matching numbers greater than 900 are considered as excellent match.[43] The method started with an initial temperature of 40 °C then 5 minutes holding time and a ramp of 5 °C min^{-1} until 180 °C was used. Helium flow was 1 mL min^{-1} and split ratio was 30:1. The inlet temperature was held at 230 °C. The injection volume was 1 microliter. An HP5 MS Capillary Column (30 m x 0.25 um x 0.25 um) was used in the instrument (Figure 4.3). Gas Chromatography–Thermal Conductivity Detection (GC-TCD Hewlett Packard 5890 Series II) was performed for gas analysis with the inlet temperature of 100 °C, initial oven temperature of 35 °C and detector temperature of 140 °C. The initial 5 minutes holding time, followed by a ramp of 20 °C/min for 8.25 minutes and final holding time of 26.75 minutes at 200 °C was used as the method for gas analysis. The Carboxen 1000 column (2.1 mm internal diameter) was capable of detecting mixtures of permanent gases

(H_2, O_2, Ar, N_2, CO and CO_2), C_1-C_2 hydrocarbons, sulfur containing gases, formaldehyde and methanol. The volume of each injection was 50 microliters.

The concentration of each compound was determined with standard curves on HPLC and GC-TCD. CO_2 was the only observed product in gas sample. The standard curve for CO_2 was performed using nitrogen as the balance gas and 5, 10, 25, 50 and 75 percent by volume CO_2 (run in triplicate) was used to make the standard curve on GC-TCD. Methacrylic acid (Sigma-Aldrich), mesaconic acid (Sigma-Aldrich), citraconic acid (Acros), acetone (Fisher Scientific), acetic acid (Sigma Aldrich), pyruvic acid (Sigma-Aldrich), citric acid, itaconic acid and 2-hydroxyisobutyric acid standard curves were made using DI water as the solvent. Five different concentrations of each compound based on grams per liter DI water were used to make the standard curves on HPLC.

4.5. Catalyst Characterization

After each reaction the catalyst was collected using a filter paper and washed with DI water. After washing with DI water, the catalyst was dried for one hour in 105 °C drying oven.

4.5.1. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) Analysis

BET theory, which explains multilayer molecular adsorption, was adopted to determine the surface area of the catalysts. The volume and relative pressure of an adsorbed gas (physical adsorption) on the surface of the catalyst are used to perform surface area calculations:

$$\frac{1}{v\left(\frac{p_0}{p}-1\right)} = \frac{c-1}{v_m c}\left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \qquad \text{Eq. (5)}$$

p_0 = Saturation Pressure

p = Equilibrium Pressure

v_m = Volume of Monolayer

c = BET Constant

v = Volume of Adsorbed Gas

From slope and intercept of Equation 5, v_m (volume of monolayer) is determined and surface area is calculated through the following equation using Avogadro's number (N), effective cross-sectional area of one adsorbate molecule (S), molar volume of the adsorbate gas (V), mass of sample (m) and volume of monolayer v_m:

$$S_{BET} = \frac{N\,S\,v_m}{m\,V} \qquad \text{Eq. (6)}$$

Therefore, a 7-point BET analysis was performed with a relative pressure of 0.05 to 0.35 (linear part of the curve) to determine surface area of the catalysts with adsorption of nitrogen gas in a Quantachrome Autosorb-1C.

BJH analysis was also performed to determine pore size distribution, average pore size, and total pore volume using N_2 desorption curves. Modified Kelvin equation is applied to perform BJH analysis (Equation 7). Prior to these analyses, samples were degassed at 250 °C-280 °C for 2 to 3 hours.

$$\ln\left(\frac{p_0}{p}\right) = \frac{2\sigma V_0\,\cos\varphi}{(\overline{r}-t)RT} \qquad \text{Eq. (7)}$$

p_0 = Saturation Pressure

p = Equilibrium Pressure

σ = Surface Tension of Fluid

$t = 7.34\,(\ln(\frac{p_0}{p}))^{-1/3}$ Film Thickness

T = Temperature

R = Universal Gas Constant

V_0 = Pore Volume

$\bar{r} = t + 8.83\,(\ln\left(\frac{p_0}{p}\right))^{-1}$ Pore Radius

4.5.2. TGA Analysis

Coke formation was determined using a METTLER-TOLEDO TGA/SDTA 851e. A method of 50 mL min^{-1} air with a ramp of 10 °C min^{-1} from 25 °C to 500 °C was used. The amount of coke on the catalysts after the reaction was determined compared to mass loss of the untreated catalyst (before reaction).

4.6. Statistical Analysis

Statistical analysis of significance was performed using R software version 3.2.1 for yields of each by-product as a function of catalyst mass. Standard deviations were calculated using data from repeated reactions. Blank reactions, reactions in presence of fermentation residuals, palladium catalyst, 0.125 g and 0.25 g hydrotalcite catalyst were replicated in each reaction condition. Error bars represent standard deviation of the mean.

4.7. Experimental Plan

Synthesis of methacrylic acid was optimized across different variables. The effect of residence time, catalyst mass, reaction temperature and substrate concentration on methacrylic acid yield was determined. The initial sets of reactions were performed with 20 g L^{-1} of substrate (in DI water) at 250 °C and 1 g catalyst. Acid and base catalysts

(Hydrotalcite, Gamma-Al_2O_3 and SiO_2–Al_2O_3) were tested for each substrate. In order to determine the effect of subcritical water only (in absence of catalyst), a set of blank reactions was also performed in varying substrate concentrations (5, 10, 20, 30 g L^{-1}) and temperatures (200, 225 and 250 °C for itaconic acid and citric acid, 200, 225, 250 and 275 °C for 2-hydroxyisobutyric acid). After determining the best catalyst in formation of methacrylic acid from each substrate, the effect of temperature (200-250 °C for itaconic acid and citric acid, 200-275 °C for 2-hydroxyisobutyric acid) and catalyst mass (0.125.0.25,0.5, 1g) was also determined. At 20 g L^{-1} and 250 °C catalyst reuse reactions and reactions in presence of palladium on hydrotalcite catalyst were performed. Finally, after determining the effect of substrate concentration (5, 10, 20, 30 g L^{-1}) at optimized catalyst mass and temperature, the effect of fermentation media residuals on methacrylic acid yield was determined for each substrate. Previously, Zhang et al. 2008 studied the effect of fermentation media residuals from glucose to lactic acid and further hydrogenation of lactic acid to propylene glycol with ruthenium in the presence of 0.1 M sodium hydroxide, 0.04 M sodium sulfate, 0.04 M sodium phosphate dibasic, 0.06 M glucose and 0.12 wt% albumin.[44] In order to determine the effect of fermentation media residuals on methacrylic acid yield these concentrations of fermentation residuals were added to the reaction medium and tested under the best conditions. Figure 4.4 shows the summary of the experimental plan in a flowchart.

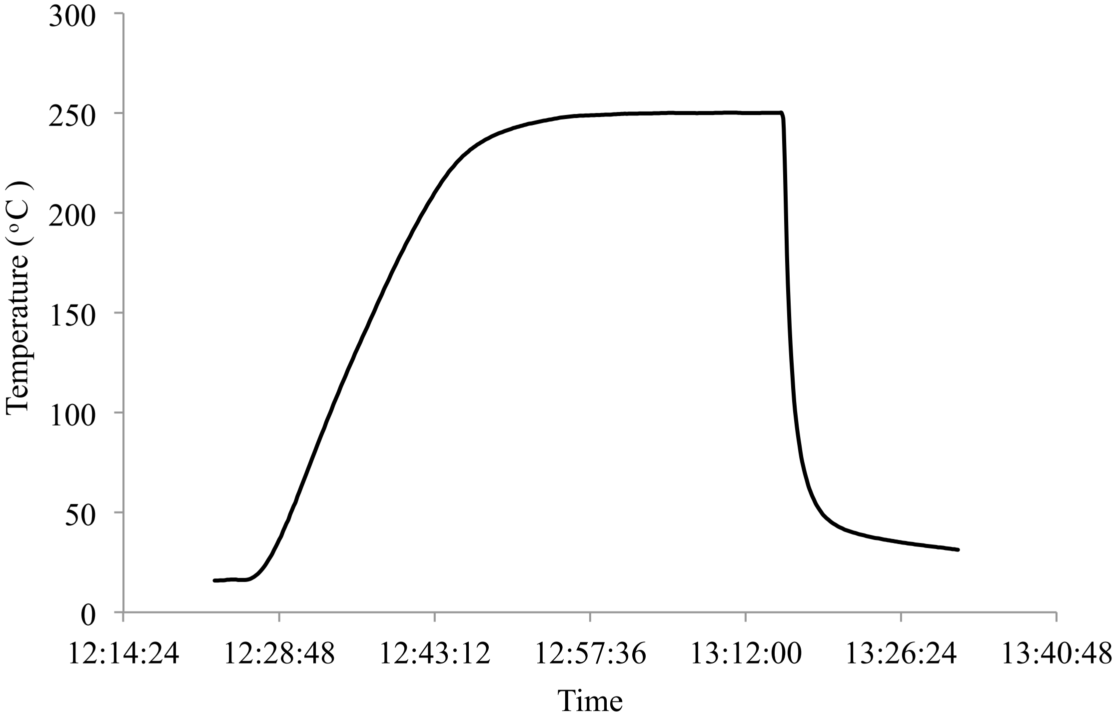


Figure 4.1: Temperature versus time plot for a performed reaction (condition: 250 °C, 15 minutes, 20 g L^{-1} citric acid, 0.125 g hydrotalcite)

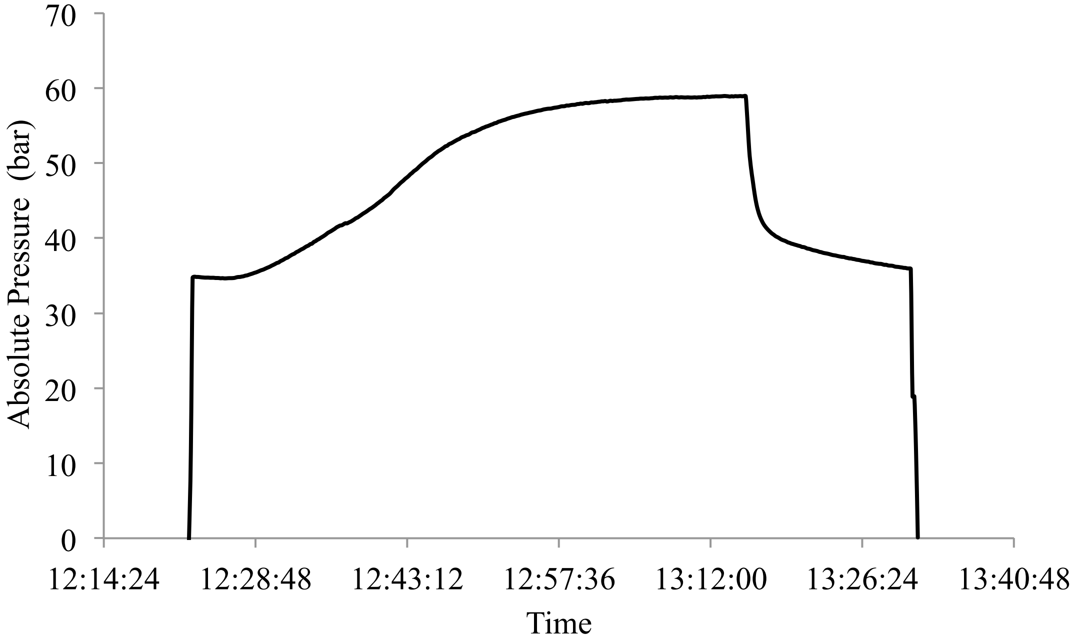


Figure 4.2: Absolute pressure versus time plot for a performed reaction (condition: 250 °C, 15 minutes, 20 g L^{-1} citric acid, 0.125 g hydrotalcite)

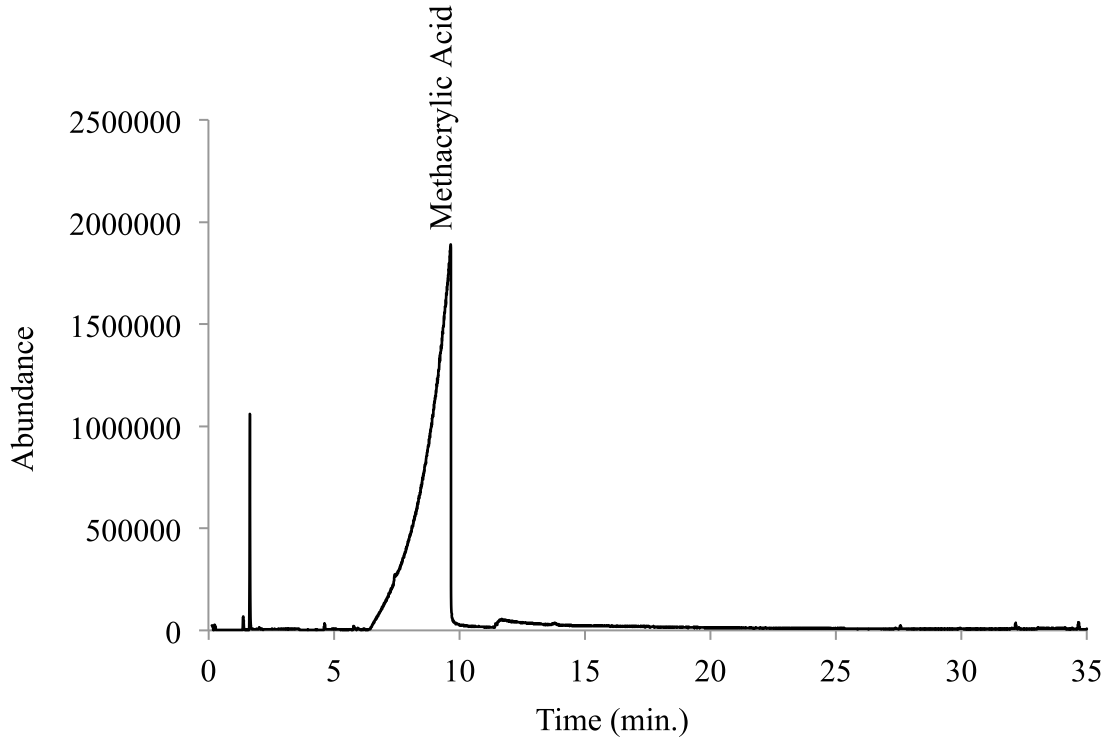


Figure 4.3: GC-MS graph (TIC) indicating the formation of methacrylic acid. The first three estimations with R-matches of 932, 914 and 903 and probability of 65% were found for the methacrylic acid peak (Condition: 20 g L^{-1} 2-hydroxyisobutyric acid, 250 °C, 15 minutes residence time)

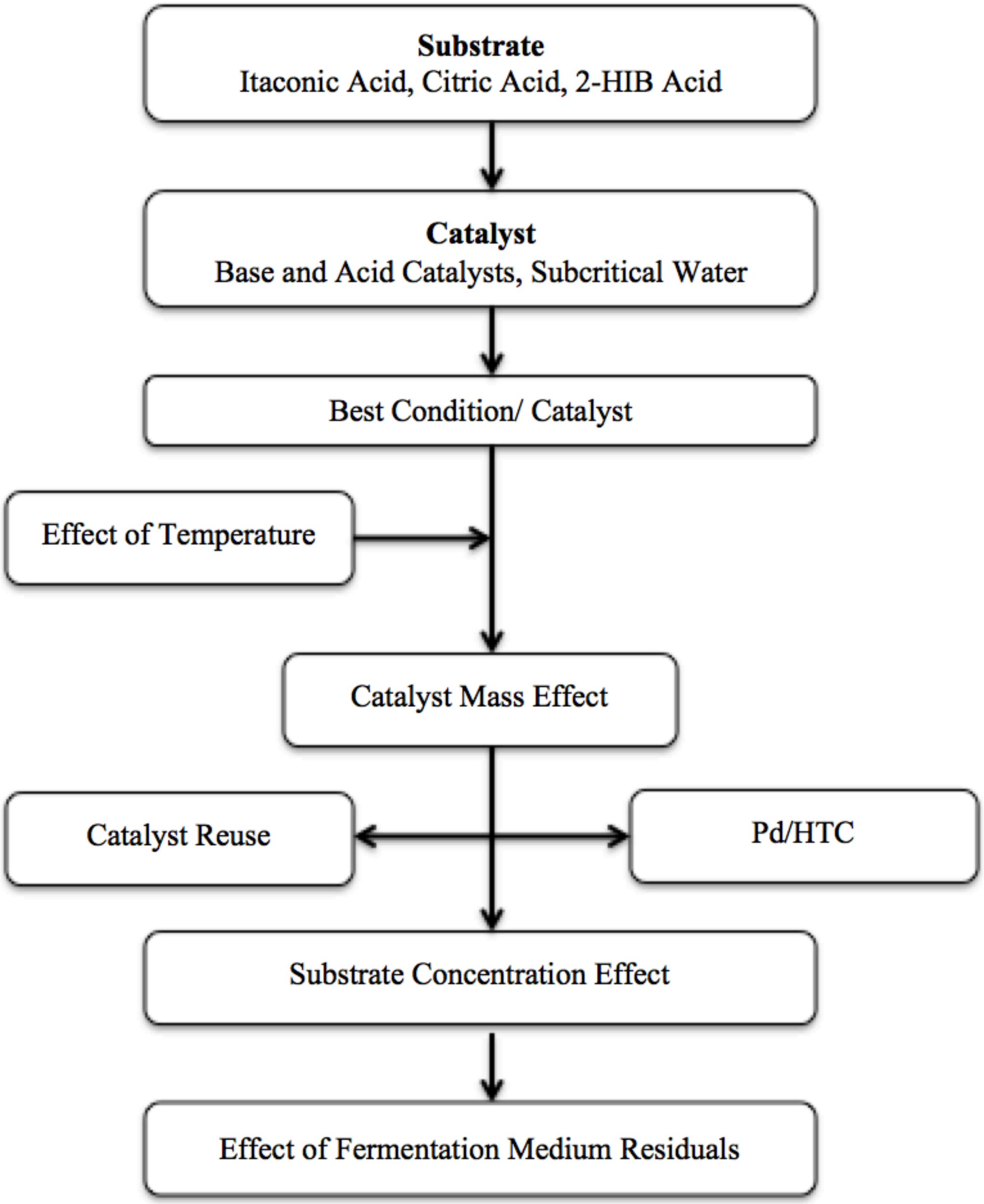


Figure 4.4: The Experimental plan flowchart

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Decarboxylation of Citric Acid to Methacrylic Acid

Among citric acid, itaconic acid and 2-hydroxyisobutyric acid, citric acid is the most available fermentation-derived substrate. Total production of citric acid in the world was around 1.6 million tons per year in 2007.[28] Citric acid requires one-step dehydration followed by two decarboxylation steps to generate methacrylic acid (Figure 2.1). Thus, the kinetics of methacrylic acid formation from citric acid over varying temperatures, substrate concentrations, residence times and catalysts were studied. The initial series of experiments were performed with hydrotalcite (calcined at 400 °C), Pd on activated carbon (Pd/C) and synthesized iron oxide on activated carbon (Iron oxide/C) catalysts. The reactions were performed at temperatures of 200, 225, 250 °C and for a one hour residence time. The feedstock solution contained 20 g L^{-1} citric acid and 0.15 M NaOH. The reason for adding NaOH in the experiments was to determine the effect of pH change in reaction medium. According to Le Nôtre et al. 2014, pH of the reaction medium effects on methacrylic acid selectivity. At low base concentrations, methacrylic acid degradation can also occur due to addition of water molecules across the double bonds.

Figure 5.1 shows that at 200 °C the methacrylic acid yield in the presence of hydrotalcite is zero. Results of control experiments (with homogeneous base) indicate higher yields of methacrylic acid in comparison with catalytic experiments at 200, 225 and 250 °C. The results verify that methacrylic acid yield increases with increasing temperature in both blank and catalytic experiments.

Unfortunately, we were not able to repeat Le Nôtre et al. 2014 results (65% MAA yield) with the palladium on carbon catalyst, and none of the other catalysts resulted in a methacrylic acid yield equal to or greater than 0.15 M of only sodium hydroxide in the reaction medium. This lower methacrylic acid yield in presence of heterogeneous catalysts might be attributed to the natural pH of these heterogeneous catalysts in reaction media since methacrylic acid formation is highly dependent on pH of reaction.

Since hydrotalcite is a solid-base catalyst and the highest methacrylic acid yields were achieved at 250 °C, a set of experiments with no base in reaction medium at different amounts of hydrotalcite (calcined at 400 °C) with temperature of 250 °C was also performed on citric acid. The results indicate that methacrylic acid yield increases with decreasing amount of catalyst in the reaction medium (Figure 5.2). The highest yield of methacrylic acid (20.7%) was achieved in presence of 0.125 g hydrotalcite. It is notable that blank reactions (substrate in water without sodium hydroxide) had lower methacrylic acid yields than all of the catalytic reactions except for reactions in presence of 1 g catalyst.

The results in Figure 5.2 also indicate that methacrylic acid formation occurs rapidly and it does not change remarkably with increasing residence time. Increasing methacrylic acid yield (Figure 5.2) with decreasing amount of hydrotalcite might be due to the basicity of hydrotalcite in reaction medium as Le Nôtre et al. 2014 reported an optimum amount of base in the reaction medium where methacrylic acid yield reaches to its highest value. The effect of adding a homogeneous base catalyst to blank reactions in different residence times also indicates that adding 0.15 M of sodium hydroxide to the reaction medium causes a dramatic increase in methacrylic acid yield (Figure 5.3).

The highest yield achieved by adding sodium hydroxide to reaction medium was 28% (after 30 minutes residence time). It is notable that at 15 minutes residence time methacrylic acid yield for both homogeneous (0.15 M sodium hydroxide) and heterogeneous (0.125 g hydrotalcite) base catalysts was above 20% (20.31% for homogeneous base catalyst and 20.69% for heterogeneous base catalyst). The one minute residence time experiments also show promising results (based on methacrylic acid yield) for production of methacrylic acid using homogeneous and heterogeneous base catalysts in a continuous reactor system. Due to severe problems such as corrosion of reactors, difficult separation and recycling of the catalyst and wastewater treatment, solid base catalysts are always preferred over homogeneous base catalyst. Results for reactions with 15 minutes residence time for both homogeneous and heterogeneous catalysts are shown in Figure 5.4 specifically. Results in Figure 5.4 clearly indicate that at the 15 minute residence time, methacrylic acid yield in the presence of 0.15 M sodium hydroxide is obtainable by applying 0.125 g hydrotalcite in reaction medium instead.

Itaconic acid, mesaconic acid, citraconic acid, acetone, acetic acid and pyruvic acid are the liquid byproducts that were determined by HPLC analysis. Yield of each byproduct versus catalyst mass is shown in Figure 5.5 for reactions at 250 °C and 1 minute residence time. Data analysis in Figure 5.5 indicates that acetic acid and citraconic had the highest yields among all byproducts. Figure 5.5 also shows that itaconic acid and its isomers yields (mesaconic acid and citraconic acid) decrease with increasing number of base sites (the same trend was observed for methacrylic acid yield). Analysis of significance (p-value) for citraconic acid, mesaconic acid and itaconic acid resulted the probability of 0.00401, 0.00989 and 0.0073, respectively. These probabilities are an indication of statistically different yields with level of 0.01. Figure 5.6 also indicates that citric acid conversion is higher for reactions with lower amount of catalyst. The higher conversion of citric acid with lower amount of catalyst might be attributed to the reduced number of base sites, similar to Li and Brill 2001 who reported that itaconate monoanion decarboxylates much faster than neutral or itaconate dianion. Since citric acid is a tricarboxylic acid and has an approximately similar structure to itaconic acid the change in pH might affect the decarboxylation of citric acid via a similar mechanism. Results clearly indicate that higher citric acid conversion results in higher methacrylic acid yield. At higher amounts of catalyst other reactions such as decarbonylation and dehydration steps might be dominant in the reaction medium. These reactions result in byproducts such as acetic acid, acetone and pyruvic acid.

As it was mentioned in the previous paragraph, itaconic acid, mesaconic acid, citraconic acid, acetone, acetic acid, pyruvic acid and methacrylic acid are the significant products of citric acid reactions in liquid phase and carbon dioxide is the only significant product in the gas phase. A carbon balance in both liquid and gas phase was performed on reactions with and without homogeneous and heterogeneous catalysts. Results indicate that blank reactions and reactions with homogeneous catalyst (0.15 M NaOH) have the highest recovered carbon of 66% and 72 % respectively (Figure 5.7). Figure 5.7 indicates the lowest percent carbon recovered in the reaction with 0.5 g hydrotalcite (calcined at

400 °C). This lower recovered carbon might be attributed to the residual carbon atoms (coke formation) on catalyst after reaction since the carbon balance was only performed on liquid and gas samples. Coke formation of this hydrotalcite catalyst was measured through TGA combustion and resulted in a coke level of 13.6 %. TGA results are shown in Figure 5.8. Higher conversion of citric acid in reactions with 0.125 g hydrotalcite results in higher yield of byproducts and methacrylic acid.

In order to study the reusability of hydrotalcite catalyst, 0.7 g out of 1 g hydrotalcite was recovered after the reaction. The recovered catalyst was reused under the same reaction condition as the fresh catalyst. Figure 5.9 indicates that the reaction in presence of reused hydrotalcite resulted in higher methacrylic acid yield. Achieving higher methacrylic acid yield with reused catalyst is due to presence of less than 1 g hydrotalcite in reaction medium (only 0.7 g out of 1 g was recovered). In addition to the lower the catalyst amount, this higher methacrylic acid yield might be also attributed to blocked base sites on the catalyst. Carbon dioxide, resulting from the decarboxylation reaction, can adsorb at the active sites on hydrotalcite and block them from binding citric acid. The lower number of base sites on the catalyst may have resulted in the higher methacrylic acid yield. Performing catalyst characterization on fresh and reused catalyst indicate that surface area and total pore volume increased and average pore size decreased after one step reuse of the catalyst (Table 5.1). Figure 5.10, 5.11 and 5.12 show a comparison between pore size distribution, BET points and desorption points of fresh and reused catalyst. Increases in the surface area and pore volume and decrease in average pore size might be attributed to the removal of interlayer water molecules and carbon dioxide from the carbonate anion present in the brucite layer.[45] Therefore, calcination in the presence of water would prevent the change in hydrotalcite structure.[44]

In order to study the effect of citric acid concentration on methacrylic acid yield, a set of experiments with 5, 10, 20 and 30 g L^{-1} citric acid concentrations was performed at 250 °C and 15 minutes. These reactions were performed with and without 0.125 g hydrotalcite allowing us to compare the results of catalytic reactions and blank reactions at the same reaction condition. Figure 5.13 indicates that in blank reactions the methacrylic acid yield did not show a remarkable increase or decrease with increasing substrate concentration, as expected. In catalytic reactions with hydrotalcite, methacrylic acid yield increased with increasing substrate concentration. The highest methacrylic acid yield in this set of experiments, 22%, was achieved with 0.125 g hydrotalcite and 30 g L^{-1} citric acid at a 15 minutes residence time.

The results of studying the effect of citric acid concentration along with the effect of catalyst mass on methacrylic acid yield strongly imply that there is an optimum citric acid mass to catalyst mass ratio where methacrylic acid yield reaches to its highest amount. Figure 5.14 shows the maximum yield of methacrylic acid versus the citric acid/ hydrotalcite ratio (g/g). The maximum and minimum yields are achieved at ratio of 9.6 and 0.8 g citric acid/g hydrotalcite, respectively. Lower ratios (higher pH) result in a lower citric acid decarboxylation rate due to the formation of dianionated or trianionated forms of citric acid, which have much lower rates of decarboxylation. At higher ratios (lower pH) methacrylic acid yield reaches to an optimum value. At very low pH (not tested in this work), after the optimum point a decrease in methacrylic acid yield is expected due to instability of methacrylic acid in very acidic medium and low decarboxylation rate of protonated itaconic acid [46] and is similarly expected for citric acid.

As mentioned in background and literature review chapter, different calcination temperatures can affect hydrotalcite activity and base site exposure. In order to study the effect of calcination temperature on methacrylic acid formation from citric acid, two sets of experiments with hydrotalcite, calcined at 300 °C and 500 °C, were performed. Comparing the results of these two sets of experiments with experiments that were performed in presence of hydrotalcite calcined at 400 °C indicate that varying calcination temperatures of hydrotalcite does not effect on methacrylic acid yield significantly (Figure 5.15). Figure 5.15 shows the results of methacrylic acid yield for 0.125 g hydrotalcite (calcined at 300, 400 and 500 °C) at 15 minutes residence time. These reactions were also performed at 1 and 30 minutes residence time and with 0.25 g hydrotalcite (data not shown). These results imply that the transformation of citric acid to methacrylic acid might be due to a pH effect of hydrotalcite in the reaction medium and not base site exposure of catalyst.

Use of solid acid catalysts in decarboxylation reactions is reported in literature. Wang et al. 2013 reported that solid acid catalysts with Lewis acid sites are effective in selective decarboxylation of gamma-valerolactone to 1-butene.[12] Gamma-Al_2O_3 possesses Lewis acid sites, while SiO_2–Al_2O_3 possesses both Brønsted and Lewis acid sites. Hence for the purpose of citric acid decarboxylation to methacrylic acid three sets of experiments with SiO_2–Al_2O_3, gamma-Al_2O_3 and a mixture of SiO_2–Al_2O_3 and hydrotalcite in reaction medium were performed. Methacrylic acid yield in reactions with SiO_2–Al_2O_3 and Gamma-Al_2O_3 was less than 10 %. Reactions with the mixture of acid and base catalyst resulted in a methacrylic acid yield lower than base catalyst only. Figure 5.16 shows the results for 250 °C operating temperature and 15 minutes residence time. These reactions were also performed at 1 and 30 minutes residence times (Data not shown). Citric acid conversion was close to 100 % in almost all of the reactions and none of the reactions in the presence of solid acid catalysts resulted in methacrylic acid yields greater than 0.125 g of only hydrotalcite.

In order to determine the effect of fermentation medium residuals on methacrylic acid yield, the reaction with the best result conditions was chosen to repeat in the presence of fermentation impurities. A medium consisting of 0.1 M sodium hydroxide, 0.04 M sodium sulfate, 0.04 M sodium phosphate dibasic, 0.06 M glucose and 0.12 wt % albumin[44] was added to 30 g L^{-1} citric acid and 0.125 g hydrotalcite. Mesaconic acid, citraconic acid, acetic acid, pyruvic acid and acetone and very small trace of itaconic was observed after the reaction. HPLC chromatograms indicated the presence of 3 unknown by-products. A yield of 28.53% was achieved for methacrylic acid in the presence of fermentation residuals, which was higher than methacrylic acid yield without fermentation impurities (22%). Figure 5.17 indicates that in the presence of fermentation impurities lower acetic acid yield, and higher pyruvic acid yield was achieved. Complete conversion of citric acid was achieved.

5.2. Decarboxylation of Itaconic Acid to Methacrylic Acid

In the previous section, the effect of varying residence times, reaction temperatures, catalyst masses and citric acid starting concentrations on methacrylic acid formation was determined. The formation of methacrylic acid from citric acid requires one dehydration step followed by two decarboxylation steps while itaconic acid can form methacrylic acid with only one decarboxylation step (Figure 2.1). Hence for the purpose of decarboxylation of itaconic acid to methacrylic acid, a set of reactions with varying amounts of catalyst ranging from 0.125 to 2 g hydrotalcite was performed at residence times of 1,15 and 30 minutes. As Figure 5.18 indicates**,** methacrylic acid yield increases with decreasing hydrotalcite mass (the same trend was observed for reactions that were performed with citric acid). The highest methacrylic acid yield was observed at 30 minutes residence time with 0.125 g hydrotalcite (27.33 %). The lowest methacrylic acid yields were observed with 2 g hydrotalcite in reaction medium. These yields were significantly lower than yields that were achieved with reactions in absence of hydrotalcite (blank runs).

In order to compare methacrylic acid yield in blank reactions and reactions with homogeneous base catalysts, 0.15 M sodium hydroxide was added to the reaction medium. Adding sodium hydroxide to the reaction medium also caused an increase in methacrylic acid yield the highest methacrylic acid yield of 45.7 % was achieved after 30 minutes (Figure 5.19). Figure 5.20 shows methacrylic acid yield in presence of varying masses of hydrotalcite and 0.15 M NaOH at 15 minutes residence time. The highest yield of methacrylic acid (39.5 %) was achieved by 0.15 M sodium hydroxide (higher than 0.125 g hydrotalcite, 22.94%).

Mesaconic acid, citraconic acid, acetone, acetic acid and pyruvic acid were the byproducts of reactions with itaconic acid. These byproducts were formed due to degradation of itaconic acid through dehydration and decarbonylation processes. Carlsson et al. 1994 reported that acetone could be formed with one-step decarbonylation followed by one-step decarboxylation from itaconic acid. Yields of each byproduct for catalyst masses of 0.125, 0.25 and 0.5 g at a 1 minute residence time are shown in Figure 5.21. Citraconic acid and acetic acid yields are significantly higher than other byproducts for each catalyst mass. The yield of acetic acid decreases from 19.82% to 9.31% with decreasing catalyst mass from 0.5 g to 0.125 g (probability of 0.00686). Due to an increase in pH of the solution at higher catalyst mass, the decarboxylation reaction might occur at a slower rate than other parasitic reactions, which results in byproducts such as acetic acid, pyruvic acid. The yield of mesaconic acid increases and yield of acetone decreases with increasing catalyst amount. Pyruvic acid and citraconic acid yields reach to their lowest value in the reaction with 0.125 g hydrotalcite.

Lower amounts of catalyst in reaction medium resulted higher methacrylic acid selectivity. Parasitic reactions such as decarbonylation of itaconic acid occur slower than decarboxylation in lower amounts of catalyst. Figure 5.22 shows the selectivity of methacrylic acid in different catalyst masses at a one minute residence time. The highest methacrylic acid selectivity at a one minute residence time was achieved with 0.125 grams of hydrotalcite (19.49%). It has to be noted that selectivity and carbon balance analysis was not possible to perform for residence times higher than 1 minute in this work due to the appearance of unknown peaks and their co-elution with itaconic acid peak.

A carbon balance was also performed on reactions with itaconic acid and results indicate that in blank reactions itaconic acid and its isomers are the main source of recovered carbon in reaction medium (Figure 5.23). Figure 5.23 indicates that the main sources of carbon in the reaction with 0.15 M sodium hydroxide are itaconic acid and its isomers and methacrylic acid. The amount of recovered carbon in the blank reaction with and without sodium hydroxide was above 80%. A comparison between carbon balance results in 0.5 g hydrotalcite and 0.125 g hydrotalcite reactions indicate that carbon recovered by acetic acid, pyruvic acid and mesaconic acid is higher in the reaction with 0.5 g hydrotalcite.

Reusability studies of the hydrotalcite were also investigated for reactions with itaconic acid. 0.92 g out of 1 g hydrotalcite was recovered after the reaction. Figure 5.24 indicates that the reaction in presence of reused hydrotalcite resulted in higher methacrylic acid yield (similar to reactions with citric acid). Reusing hydrotalcite increased methacrylic acid yield from 10.13 % (achieved by fresh catalyst) to 16.94%. Achieving higher methacrylic acid yield in presence of reused catalyst might be attributed to the lower amount of catalyst amount and a lower number of base sites on hydrotalcite (blocked by carbon dioxide). The surface area, average pore size and total pore volume of the reacted hydrotalcite decreased after the first reaction as expected. Interestingly, the catalyst characterization for the reused hydrotalcite indicates an increase in surface area and total pore volume (Table 5.2). Figure 5.25, 5.26 and 5.27 show a comparison between pore size distribution, BET points and desorption points for fresh and reused catalyst, respectively. As mentioned earlier, the increased surface area and pore volume of reused hydrotalcite might be attributed to the removal of interlayer water molecules and carbon dioxide from the carbonate anion present in the brucite layer.[45]

Studying the effect of itaconic acid concentration on methacrylic acid yield indicates that in blank reactions methacrylic acid yield does not change with change in itaconic acid concentration. In reactions with 0.125 g hydrotalcite methacrylic acid yield increases from 17.6% at 5 g L^{-1} to above 22% at 20 g L^{-1} and 30 g L^{-1} (Figure 5.28). Methacrylic acid yield versus itaconic acid mass to catalyst mass ratio plot (Figure 5.29) shows that the maximum methacrylic acid yield occurs at ratio of 6.4. At higher and lower ratios, the methacrylic acid yield starts decreasing. The maximum yield in citric acid reaction occurred at a higher ratio of 9.6.

In order to determine the effect of reaction temperature on methacrylic acid yield, 2 sets of experiments with temperature ranging from 200 – 250 °C, with and without hydrotalcite in reaction medium, were performed. The results of both sets of experiments indicate an increase in methacrylic acid yield with increasing temperature from 200 °C to 250 °C. The low methacrylic acid yield at lower temperatures is due to incomplete conversion of itaconic acid at lower temperatures (Figure 5.30).

Hydrotalcite calcination temperature effect was also determined for itaconic acid reactions. Similar to citric acid reactions, methacrylic acid yield did not show a significant change with testing hydrotalcite calcined at temperatures of 300, 400 and 500 °C (Figure 5.31). Figure 5.31 shows the results for reactions that were performed at 250 °C and 15 minutes residence time. These reactions were also performed for 1 and 30 minutes residence times (data not shown).

The importance of using transition metals such as palladium- in decarboxylation of itaconic acid and to methacrylic acid has been discussed.[7] In order to determine the effect of both hydrotalcite and palladium on methacrylic acid yield, hydrotalcite impregnated with palladium catalyst was synthesized. Results of adding Pd/HTC to the reaction medium indicates that the methacrylic acid yield in presence of 0.5 g Pd/HTC is lower than methacrylic acid yield in the presence of 0.5 g hydrotalcite (Figure 5.32).

Figure 5.33 compares the results for mixture of 0.15 M sodium hydroxide and Pd/C to the results of 0.15 M sodium hydroxide only in reactions medium. These results indicate that adding palladium on carbon catalyst to the reaction medium decreased methacrylic acid yield in all of tested residence times (similar to citric acid).

Gamma-Alumina and silica-alumina catalyst were also tested on itaconic acid. Results in Figure 5.34 indicate that in reactions with gamma-alumina and silica-alumina conversion of itaconic acid and methacrylic acid yield were low. Reaction in the presence of the acid and base catalyst mixture resulted in 96% itaconic acid conversion and a methacrylic acid yield the was slightly lower than the methacrylic acid yield in presence of 0.125 g hydrotalcite only. These results imply that the solid acid catalysts have an inhibition effect on itaconic acid decarboxylation rate. This lower itaconic acid conversion might be attributed to decrease in pH with adding acid catalysts since protonated itaconic acid has lower decarboxylation rate.

The effect of fermentation medium residuals was also determined for itaconic acid and 30 g L^{-1} itaconic acid and 0.125 g hydrotalcite was tested with and without fermentation impurities. Mesaconic acid, citraconic acid, acetic acid, pyruvic acid and acetone, a very small trace of itaconic and two unknown by-products were observed after the reaction. A yield of 30.77% was achieved for methacrylic acid in presence of fermentation residuals, which was higher than methacrylic acid yield without fermentation impurities (22%). Complete conversion of citric acid was achieved for both reactions (Figure 5.35). The increase in methacrylic acid yield of both itaconic acid and citric acid reactions in presence of fermentation residuals might be due to binding of fermentation residuals to active sites and the change in pH of reaction medium.

5.3. Dehydration of 2-Hydroxyisobutyric Acid to Methacrylic Acid

Methacrylic acid formation is possible through one-step dehydration of 2-hydroxyisobutyric in subcritical water. Several sets of reactions over varying temperatures, residence times and substrate concentrations were performed to determine the kinetics of methacrylic acid formation from 2-hydroxyisobutyric acid in subcritical water. Figure 5.36 shows methacrylic acid yield versus residence time (1, 15 and 30 minutes) at temperatures of 200 °C to 275 °C. The lowest methacrylic acid yield (2.9 %) was observed at 200 °C and 1 minute residence time. As residence time increases, methacrylic yield increases to 11% at 30 minutes and 200 °C. At 225 °C the highest methacrylic acid yield was also observed at 30 minutes (48.1 %). At 250 °C, a yield of 57% at 1 minute, 65.7% at 15 minutes and 65.5% at 30 minutes was achieved. Yield of 71.48 %, the highest methacrylic acid yield, was observed at 1 minute residence time at 275 °C. At 275 °C, as time increases to 15 minutes, methacrylic acid yield decreases to 67% and with further increase in time to 30 minutes, methacrylic acid yield decreases to 65.5%. These results imply that due to a subcritical water effect and higher acidity of a reaction medium, methacrylic acid is not stable at higher temperatures and starts decomposing to byproducts, as time increases. In general, at lower temperatures (200 °C and 225 °C), methacrylic acid yield increased with increasing residence time. At 250 °C and 275 °C after 15 minutes residence time methacrylic acid yield started decreasing with increasing residence time. Due to the ion product in subcritical water, the hydronium content of the reaction medium increases with increasing temperature.[13] The higher acidity of the reaction medium results in a higher dehydration reaction rate. On the other hand, methacrylic acid is a degradable component in acidic medium. Hence the decreased methacrylic acid yield in higher temperatures might be attributed to the acidic reaction medium. Figure 5.37 shows 2-hydroxyisobutyric acid conversion versus time at temperatures of 200 °C to 275 °C. Conversion of 2-hydroxyisobutyric acid increased with increasing temperature and residence time. The lowest and highest 2-hydroxyisobutyric acid conversion was observed at 200 °C (1 minute-16.85%) and 275 °C (30 minutes-85.6%), respectively.

The effect of temperature on methacrylic acid yield was also determined (Figure 5.38). Increasing temperature from 200 °C to 275 °C increases methacrylic acid yield. At temperature between 200 °C to 250 °C, methacrylic acid yield increases with increasing residence time. At 275 °C, methacrylic acid yield starts decreasing slowly due to degradation of methacrylic acid.

Acetone, acetic acid, pyruvic acid and citraconic acid were the byproducts of 2-hydroxyisobutyric reactions and carbon dioxide was the only gas phase product. Figure 5.39 is the result of performing a carbon balance on the 2-hydroxyisobutyric acid reactions at a one minute residence time and temperatures of 200 °C to 275 °C. Figure 5.39 indicates that at 200 °C and 225 °C the highest recovered carbon is achieved by unconverted 2-hydroxyisobutyric acid in the reaction medium. At higher temperatures, 250 °C and 275 °C, methacrylic acid becomes the main product of reactions. At 250 °C and 275 °C the highest amount of carbon is recovered by methacrylic acid. It is notable that in all of the reactions, the amount of recovered carbon was above 90 %. Less than 5 % of the recovered carbon was associated with byproducts and carbon dioxide in each reaction.

In order to determine the effect of substrate concentration on methacrylic acid yield 5, 10, 15, 20, 30 g L^{-1} 2-hydroxyisobutyric acid was prepared to test at 250 °C and 15 minutes residence time. Higher concentrations of methacrylic acid were observed with increasing substrate concentration, but methacrylic acid yield did not change notably as expected (Figure 5.40). It is notable that 2-hydroxyisobutyric acid conversion also remained the same for all of these reactions (78 %).

Dehydration reactions can occur in presence of acid catalysts. Silica-alumina and gamma alumina are solid acid catalysts that contain Brønsted acid sites and Lewis acid sites, respectively. Yamaguchi et al. 1999 also reported the presence of acid sites on hydrotalcite. Active acid-base sites are obtained from the formation of Mg-O-Al bonds after calcination of hydrotalcite.[21] Hence, for the purpose of 2-hydroxyisobutyric acid dehydration, silica-alumina, gamma-alumina and hydrotalcite (calcined at 400 °C) were tested under the subcritical water condition at 250 °C. In comparison to blank reactions, reactions in presence of hydrotalcite resulted in lower 2-hydroxyisobutyric acid conversion (62 %) and hence methacrylic acid yield (53%) (Figure 5.41). Lower 2-hydroxyisobutyric acid conversion might be attributed to the inhibitory effect of hydrotalcite due to its basicity. The high basicity of the reaction medium might prevent the occurrence of dehydration process in subcritical water. A comparison between the results of acid catalyst reactions and blank reactions is presented in Figure 5.41 indicating that none of the acid catalysts resulted in a higher methacrylic acid yield compared to blank reactions. Lewis and Brønsted acid sites were not effective in dehydration process of 2-hydroxyisobutyric acid.

The effect of adding fermentation residuals to reaction media for 2-hydroxyisobutyric acid was also determined at 30 g L^{-1} 2-hydroxyisobutyric acid in presence of fermentation impurities. Figure 5.42 indicates that conversion of 2-hydroxyisobutyric acid and methacrylic acid yield were lower in presence of 0.1 M sodium hydroxide, 0.04 M sodium sulfate, 0.04 M sodium phosphate dibasic, 0.06 M glucose and 0.12 wt % albumin. Methacrylic acid yield decreased from 66.19 % to 60.39%. The lower methacrylic acid was a result of lower 2-hydroxyisobutyric acid conversion, which indicates that presence of fermentation impurities might have an inhibition effect on substrate conversion.

Citramalic acid is another intermediate, in citric acid decomposition pathway (Figure 2.1), that can form methacrylic acid with a one-step decarboxylation to 2-hydroxyisobutyric acid followed by a further dehydration step. Results of applying 0.125 g HTC in reaction medium with citramalic acid shows that hydrotalcite catalyst does not affect the methacylic acid yield (Figure 5.43). Figure 5.44 also indicates that the major products of citramalic acid reactions at 250 °C are pyruvic acid and acetic acid with yields of above 20% and 40%, respectively.

5.4. Conclusion and Future Scope

Results of using hydrotalcite in reaction medium indicate that using this solid base catalyst increases the methacrylic acid yield in decarboxylation reaction of itaconic acid and citric acid (relative to blank reactions-water only). The highest methacrylic acid yields were achieved at lowest tested catalyst amount clearly indicating that there is an optimum substrate mass to catalyst mass ratio (g/g) of 9.6 and 6.4 in decarboxylation of citric acid and itaconic acid to methacrylic acid, respectively. The reacted and reused hydrotalcite showed higher activity in comparison to the fresh hydrotalcite. These promising results concerning the reusability of catalyst also confirm that this solid base catalyst can substitute for homogeneous base catalysts, which are difficult to recycle and separate from reaction media. Using acid catalysts and transition metal catalysts was not successful in formation of methacrylic acid from itaconic acid and citric acid. Adding fermentation residuals to reaction medium resulted in higher methacrylic acid yield for both citric acid and itaconic acid.

Another potential microbial fermentation product, 2-hydroxyisobutyric acid, was also tested as a substrate in this work. 2-hydroxyisobutyric acid requires only a one step dehydration to form methacrylic acid. High yields of methacrylic acid were achieved by using 2-hydroxyisobutyric acid in subcritical water conditions. Using solid acid and base catalysts was not successful in the dehydration of 2-hydroxyisobutyric acid to methacrylic acid. The relative high conversion and methacrylic acid yields for all substrates at a one minute residence time, suggests these transformation processes can be converted from batch to continuous production in a packed bed reactor system.

It is envisioned that decarboxylation/dehydration reactions could be performed in a continuous packed bed reactor system or PFR to determine reaction kinetics, product yield and selectivity, and catalyst longevity under continuous conditions. Since our best results for itaconic acid and citric acid occurred at 250 °C and a substrate/catalyst ratio of 6.4 (itaconic cid) and 9.6 (citric acid) g /g in the batch reactor system, these temperature and ratios will be used as starting points to test the effect of operating temperature and substrate/catalyst ratio in the continuous packed bed reactor system. Effect of $\frac{\text{Concentration of Substrate}}{\text{Mass of Catalyst}}$ ratio (1 to 12 g/g), and temperature (225 °C to 275 °C) on methacrylic acid yield will be determined. In order to keep the substrate (carboxylic acid in water solution) in liquid phase during the reaction, the starting reaction pressure will be higher than the vapor pressure of water at 250 °C and other temperatures. Residence time in packed bed reactors is equal to Volume of Bed/ Flow Rate.[47] With measuring the bulk density of the catalyst and knowing the optimized mass of catalyst, we will be able to calculate the volume of catalyst bed. Therefore, with changing flow rate, liquid residence time will change. Since helium is a noble gas, it will be used as a carrier gas to the reactor.

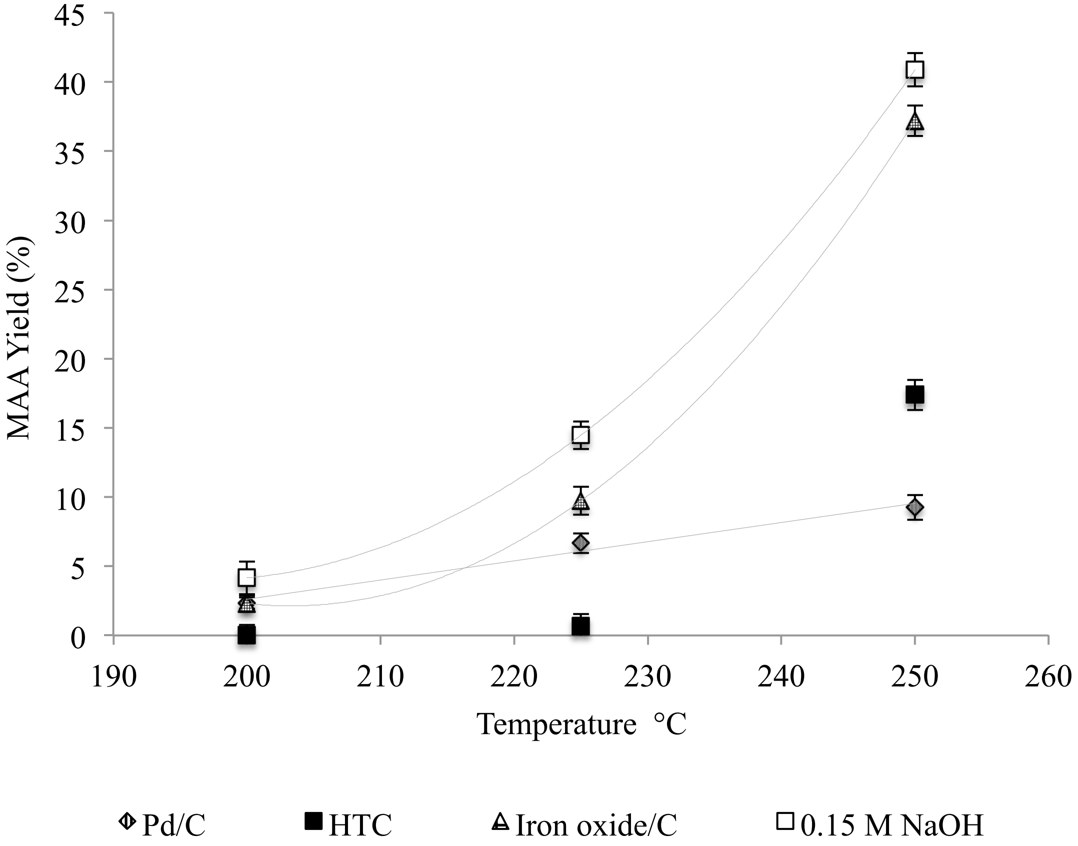


Figure 5.1: Effect of reaction temperature on methacrylic acid yield. (Reaction Condition: 20 g L^{-1} citric acid + 0.15 M NaOH, 1g catalyst, 1 hr)

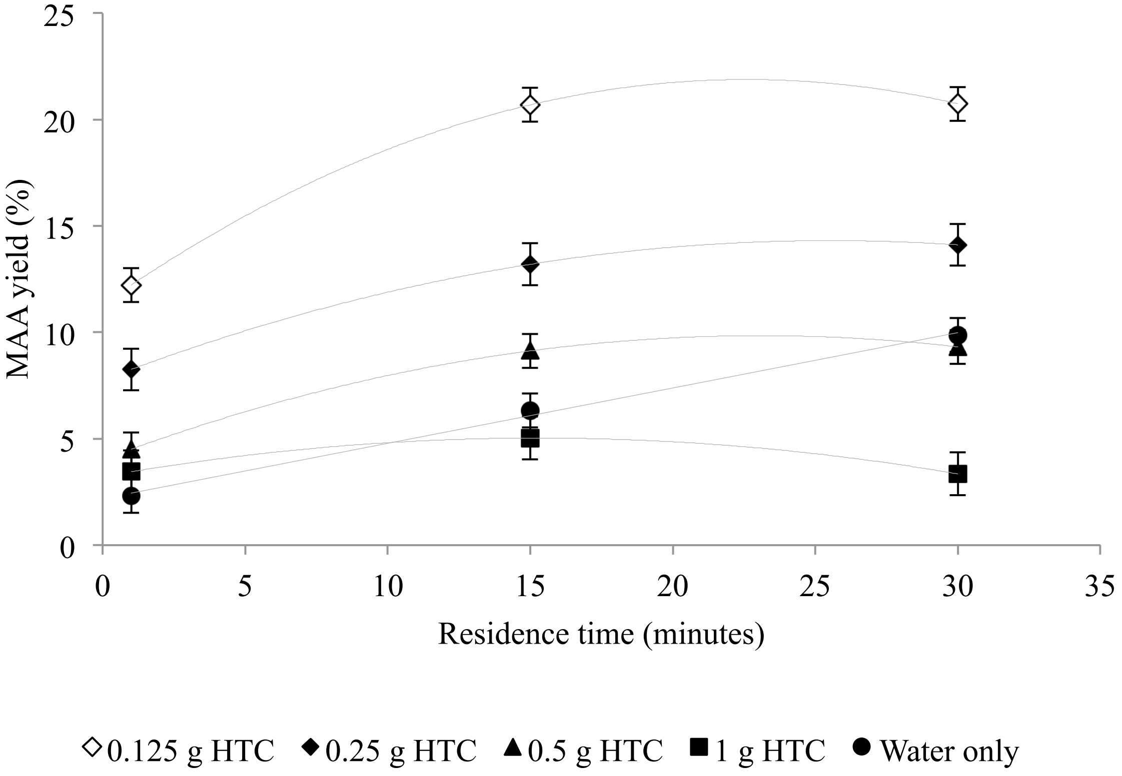


Figure 5.2: MAA yield at 250 °C, HTC calcined at 400 °C, Substrate: 20 g L^{-1} citric acid +No base. Blanks were in presence of substrate and water.

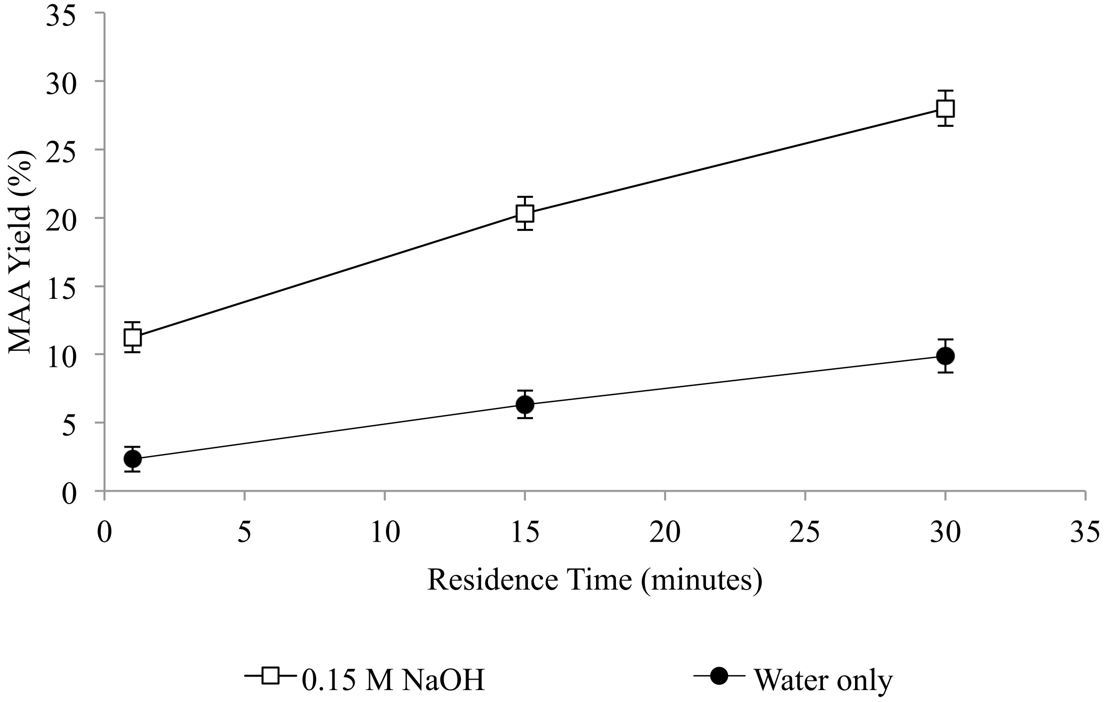


Figure 5.3: A comparison between methacrylic acid yield in blank reactions with and without sodium hydroxide (250 °C-0.15 M NaOH-20 g L^{-1} citric acid)

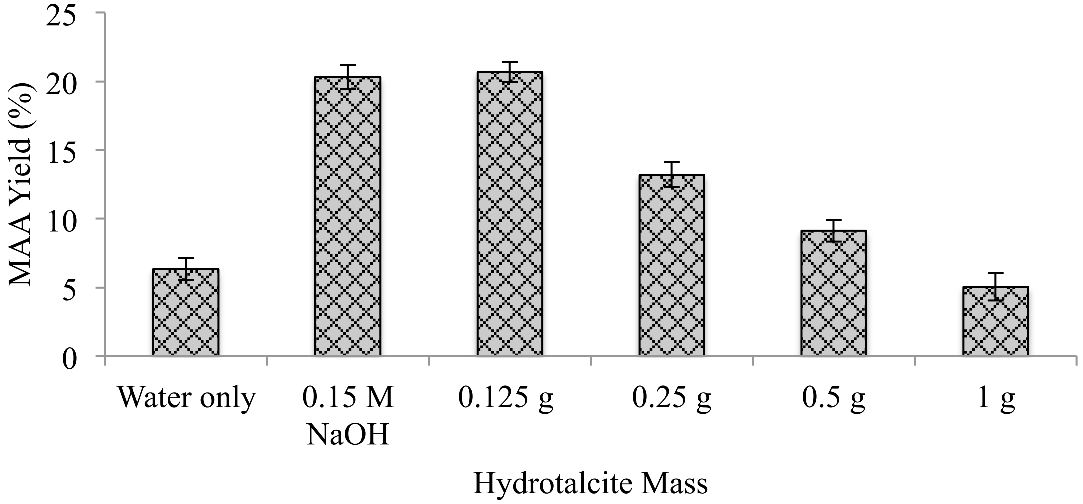


Figure 5.4: Methacrylic Acid (MAA) yield at 250 °C (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} citric acid, Residence Time: 15 min)

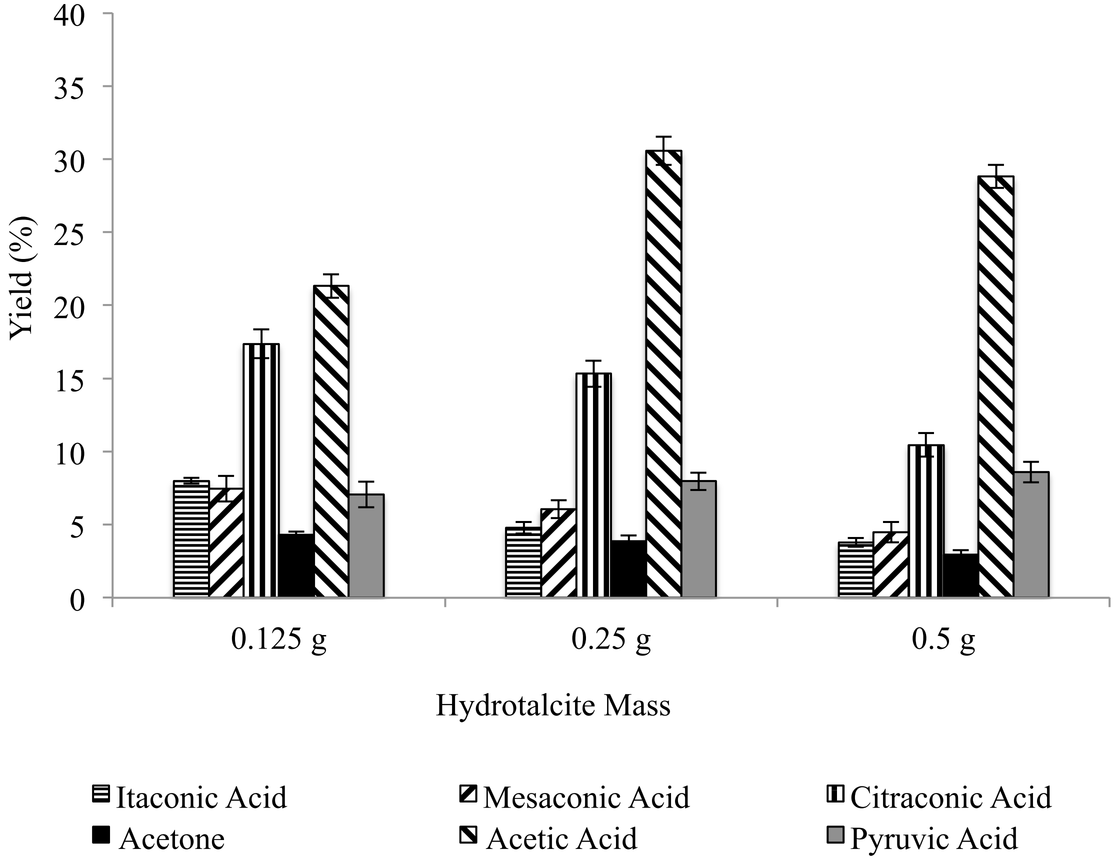


Figure 5.5: Byproduct yields at different hydrotalcite (calcined at 400 °C) masses for conversion of citric acid (20 g L^{-1} citric acid, 1 min and 250 °C)

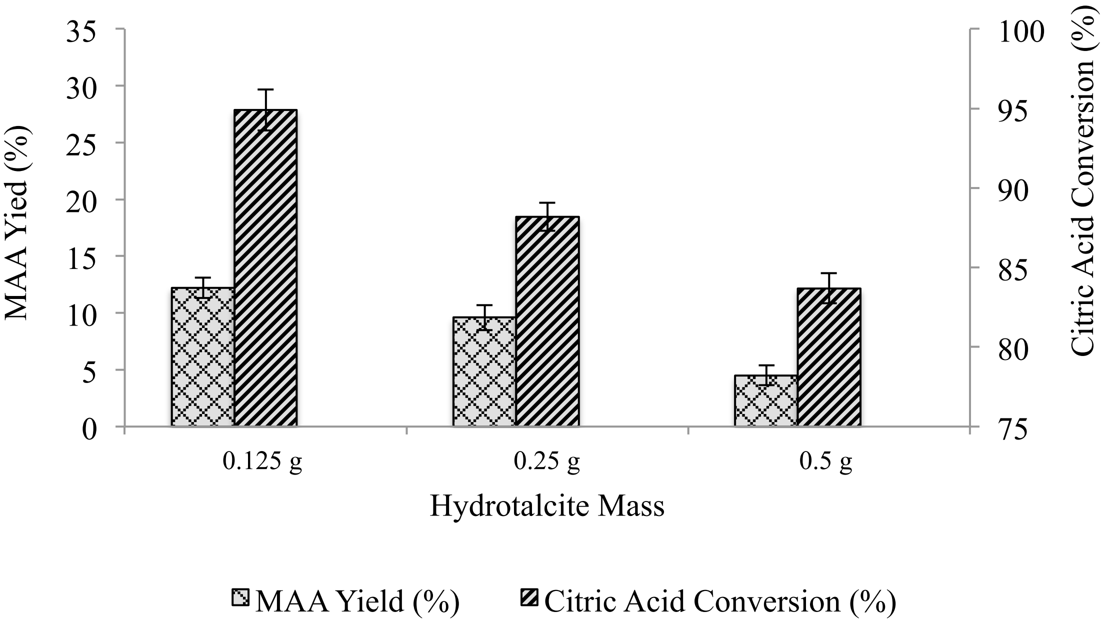


Figure 5.6: MAA yields and citric acid conversion at 250 °C (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} citric acid, 1 min)

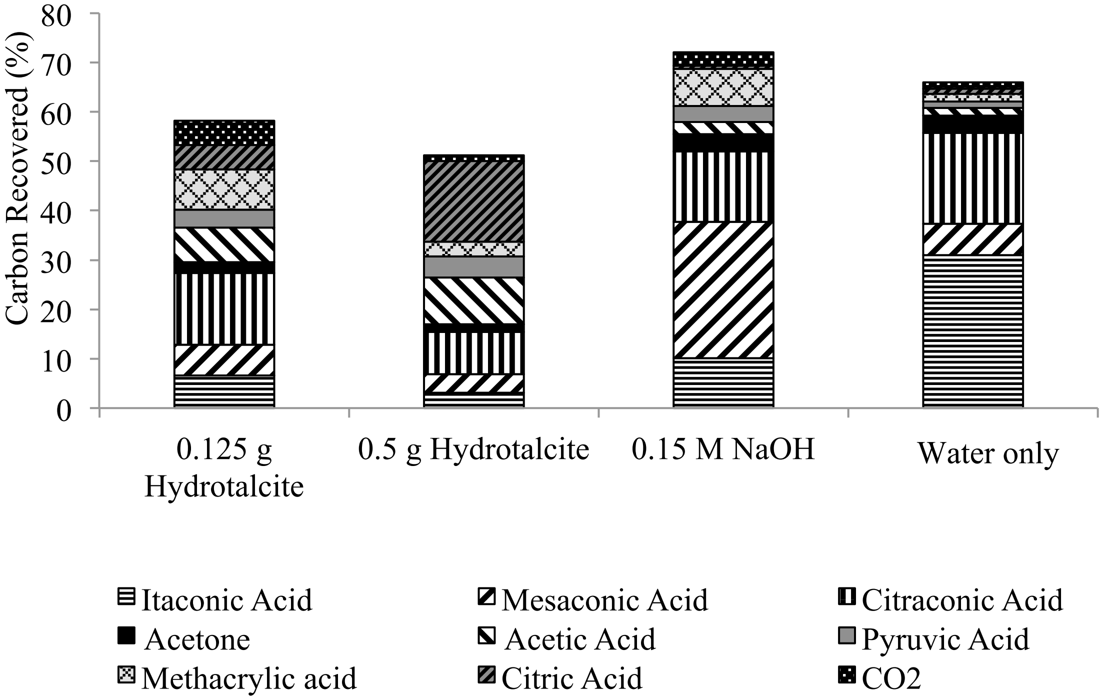
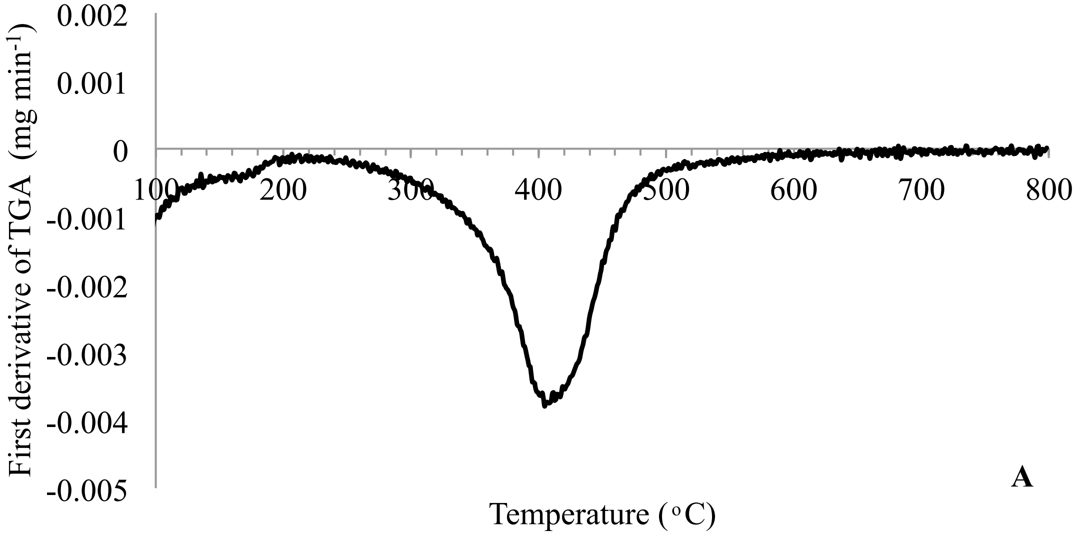


Figure 5.7: Carbon balance for citric acid reactions (reaction condition: 250 °C, 1 min, 20 g L^{-1} citric acid)



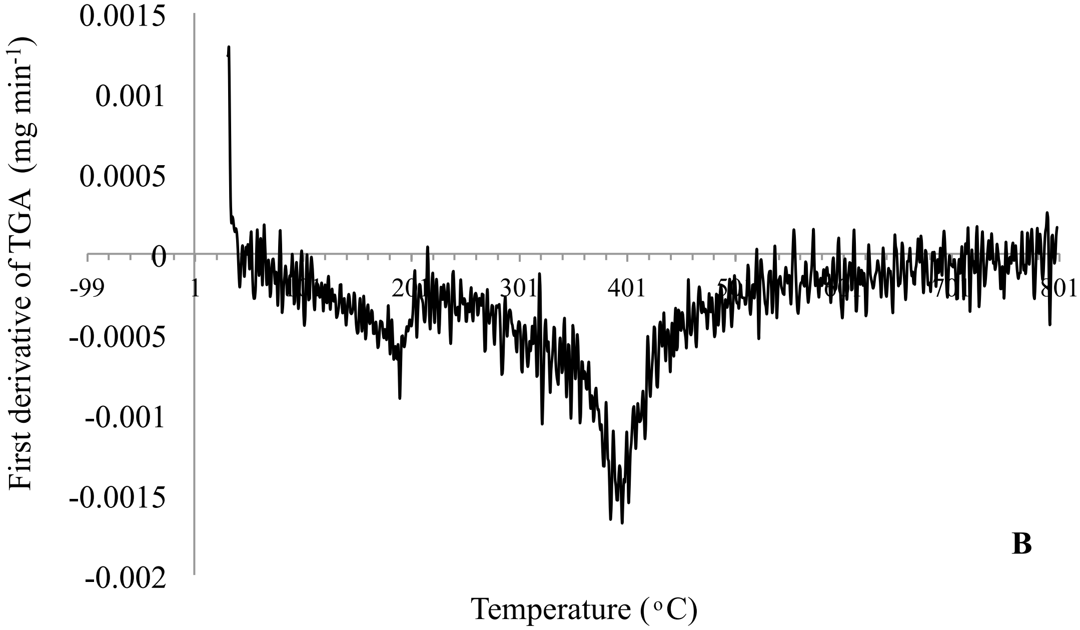


Figure 5.8: TGA analysis data. (A) Reacted hydrotalcite. Condition: (250 °C, 1 min, 20 g L^{-1} citric acid). (B) Fresh hydrotalcite

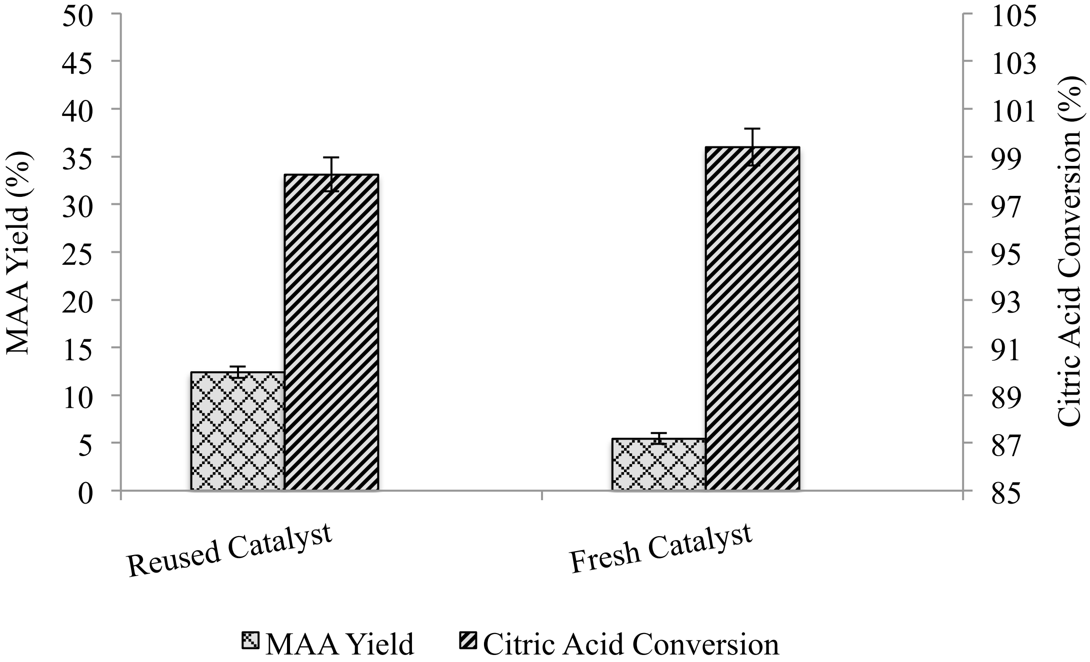


Figure 5.9: Effect of adding reused hydrotalcite on MAA yield (1 g fresh hydrotalcite, 0.7 g recovered hydrotalcite, 250 °C, 20 g L^{-1} citric acid, 15 minutes)

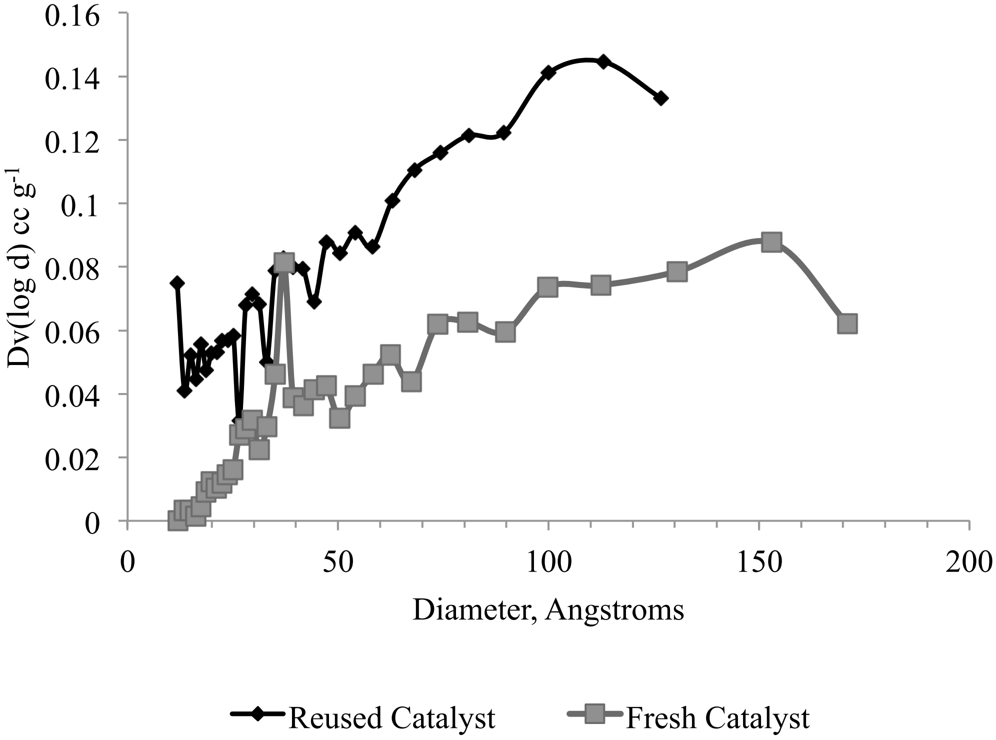


Figure 5.10: Pore size distribution of fresh and reused hydrotalcite. (Condition: 0.7 g recovered hydrotalcite, 250 °C, 20 g L^{-1} citric acid, 15 minutes)

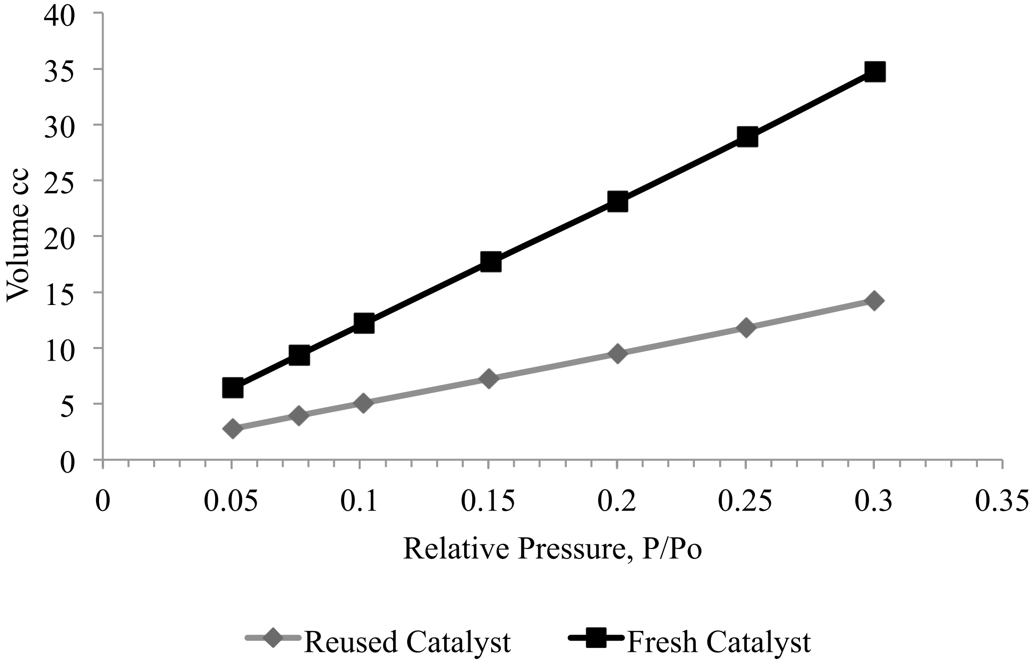


Figure 5.11: BET points for fresh and reused hydrotalcite. **(**Condition: 0.7 g recovered hydrotalcite, 250 °C, 20 g L^{-1} citric acid, 15 minutes)

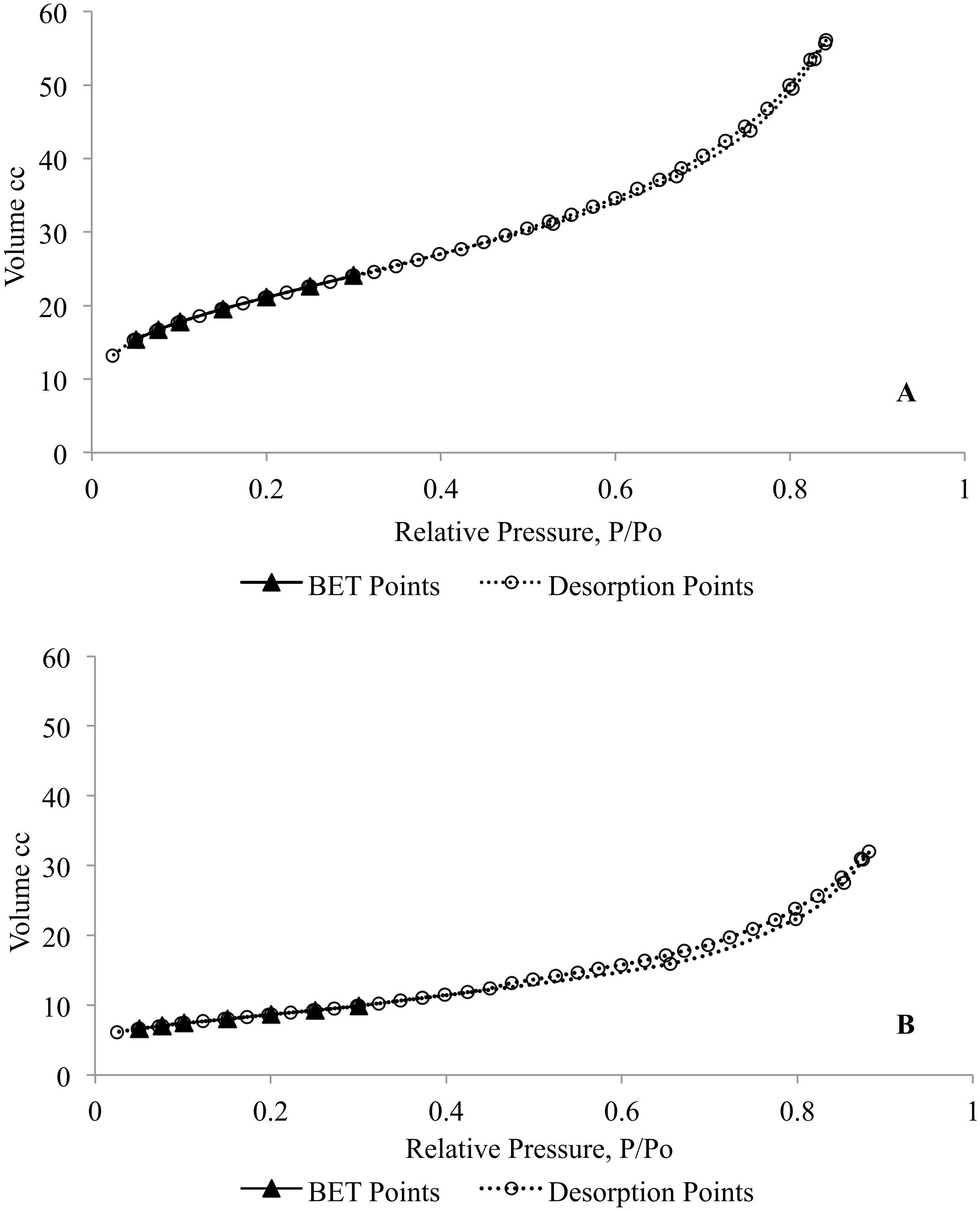


Figure 5.12: Isotherms of fresh (B) and reused (A) hydrotalcite. **(**Condition: 0.7 g recovered hydrotalcite, 250 °C, 20 g L^{-1} citric acid, 15 minutes)

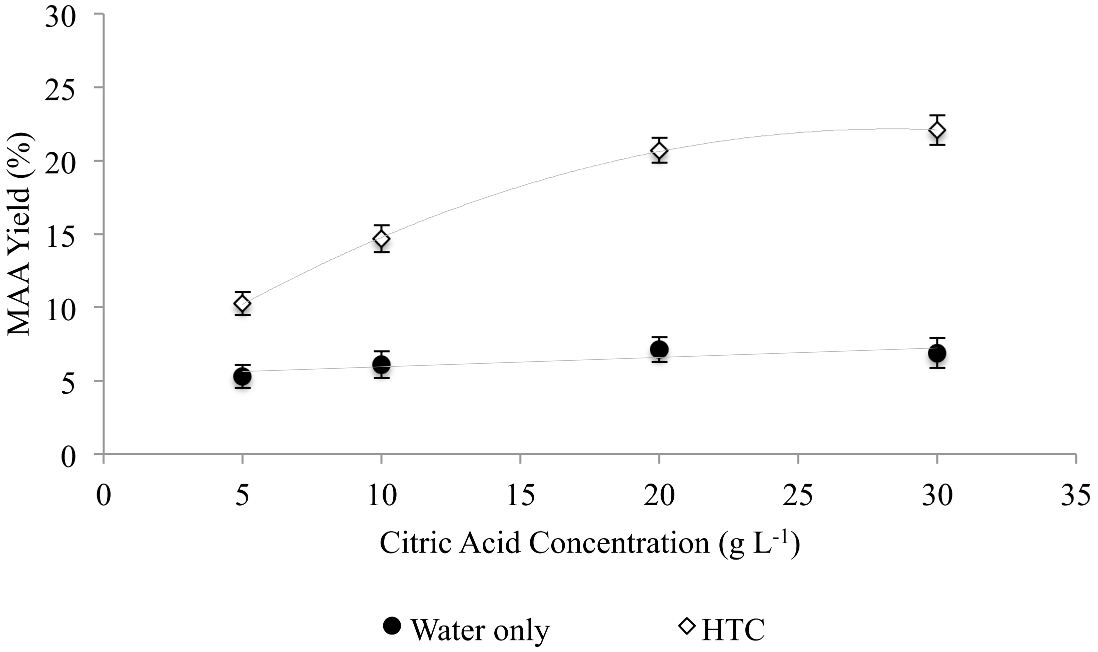


Figure 5.13: Effect of substrate concentration on MAA yield in blank and catalytic (0.125 g HTC calcined at 400 °C) reactions (250 °C, 15 minutes)

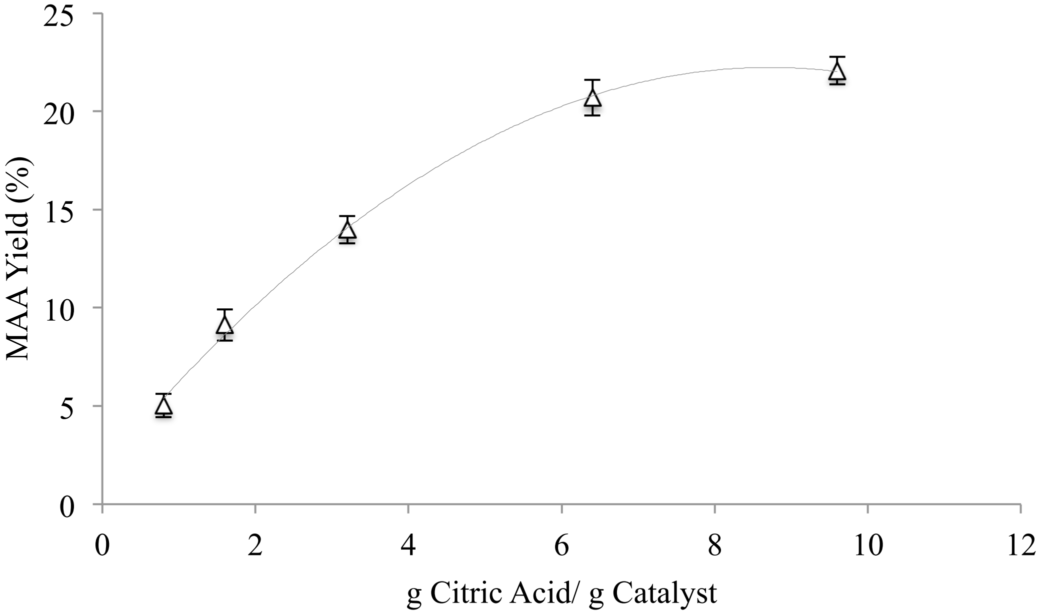


Figure 5.14: Optimum g citric acid/g hydrotalcite ratio (Condition: 250 °C, 15 minutes, hydrotalcite calcined 400 °C)

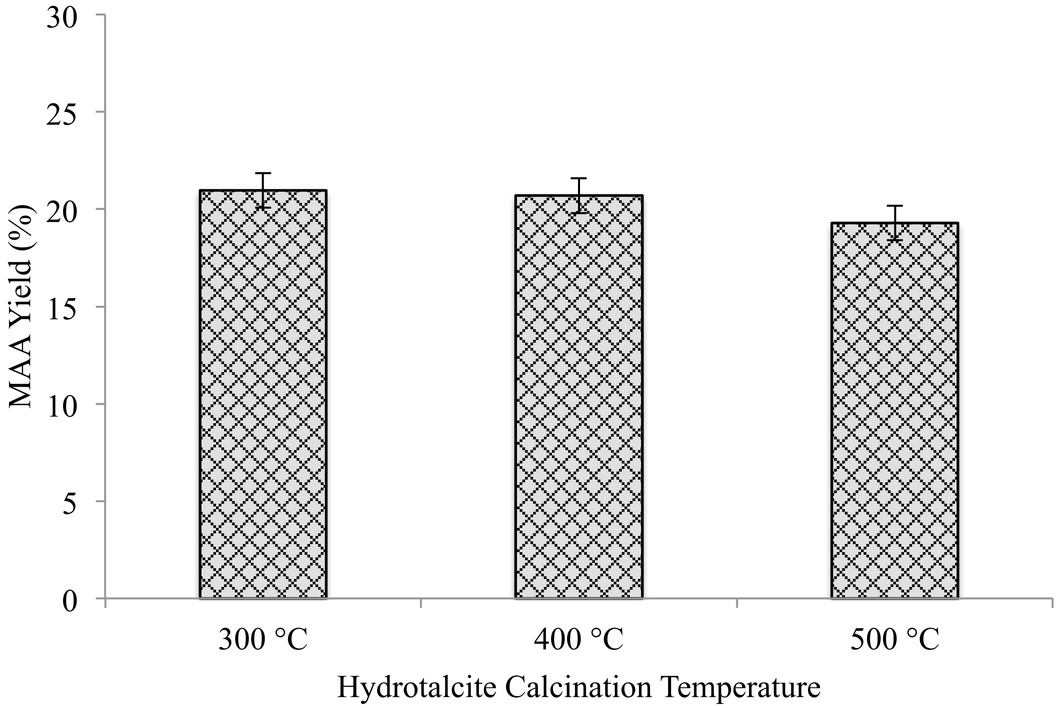


Figure 5.15: MAA yield at 250 °C, Substrate: 20 g L^{-1} citric acid, Residence Time: 15 min, Catalyst Amount: 0.125 g

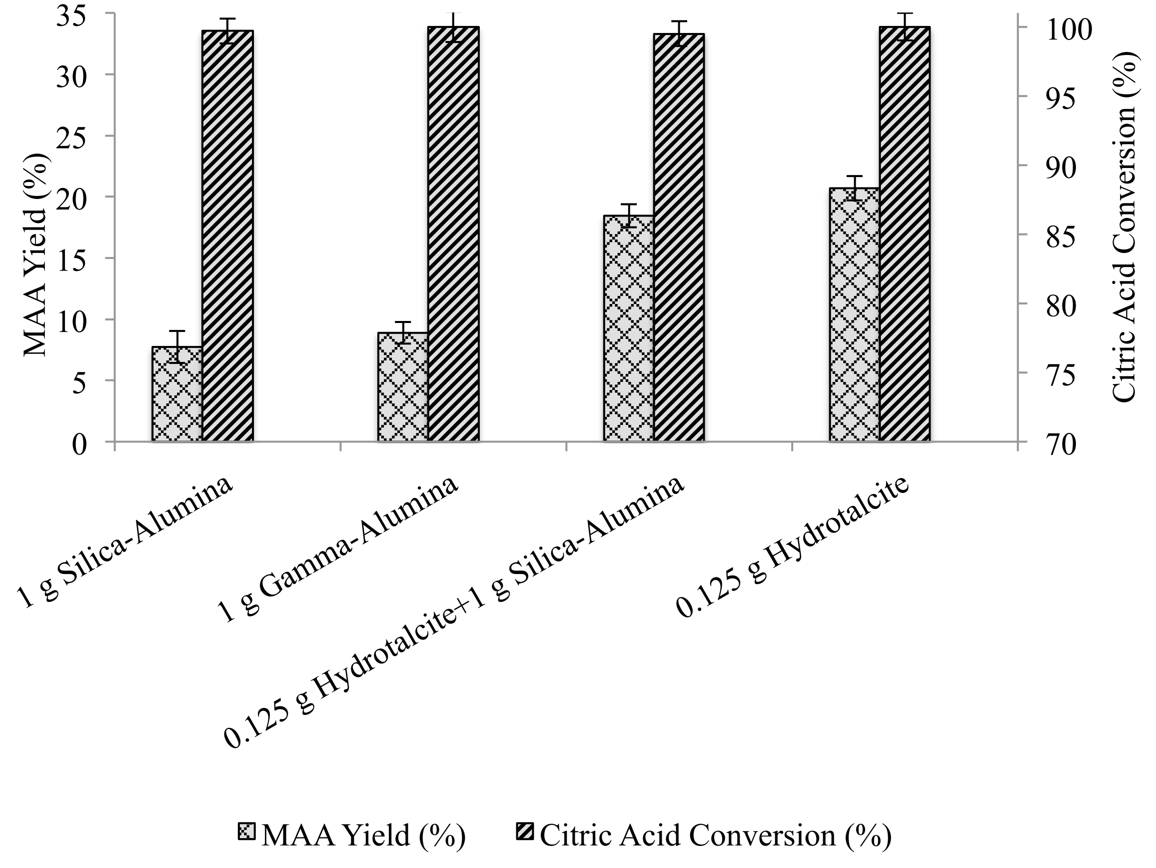


Figure 5.16: Effect of using acid catalyst on MAA yield (250 °C, Substrate: 20 g L^{-1} citric acid, Residence Time: 15 min- hydrotalcite was calcined at 400 °C)

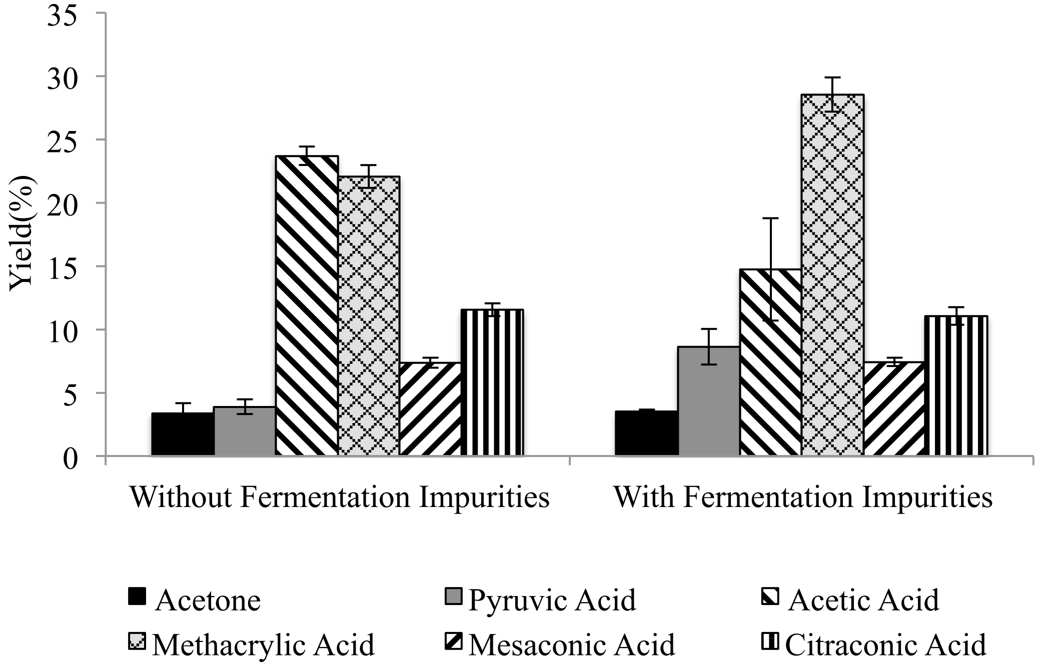


Figure 5.17: Effect of fermentation impurities on methacrylic acid and byproducts yield (Condition: 250 °C, Substrate: 30 g L^{-1} citric acid, Residence Time: 15 min- 0.125 g hydrotalcite calcined at 400 °C)

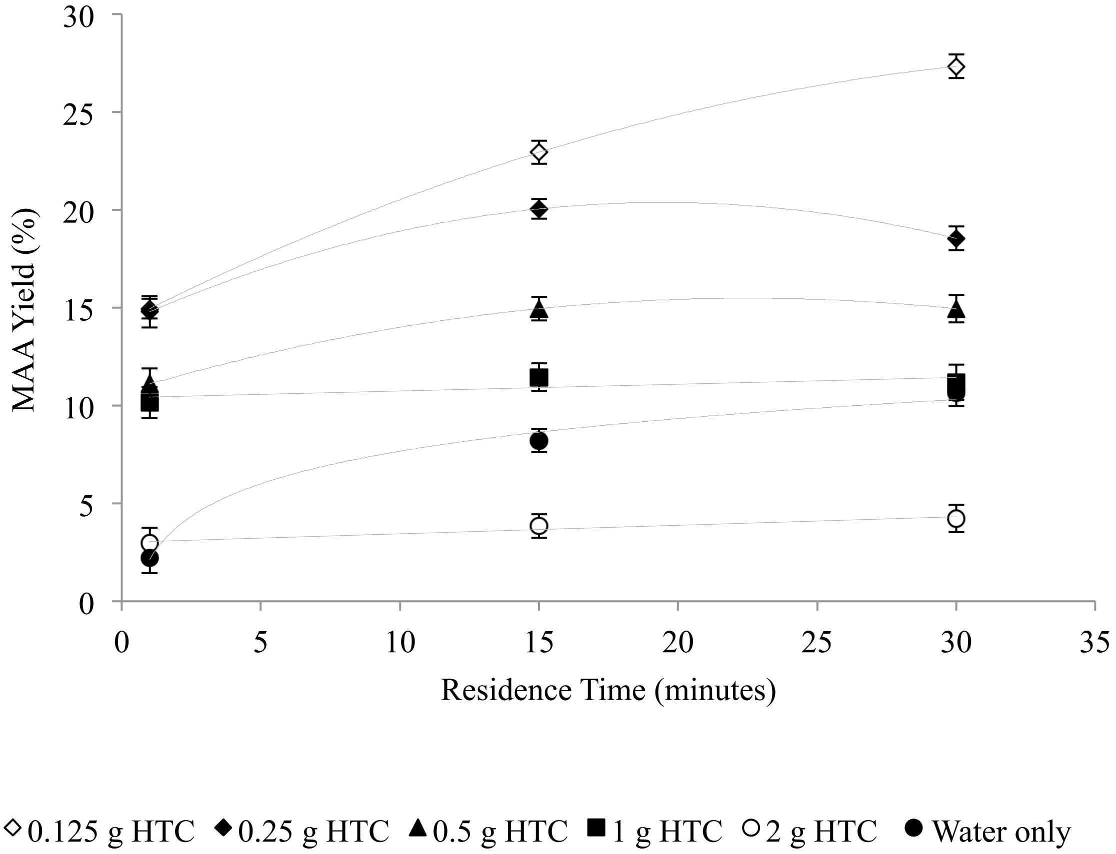


Figure 5.18: MAA yield at 250 °C (Substrate: 20 g L^{-1} itaconic acid +No base)

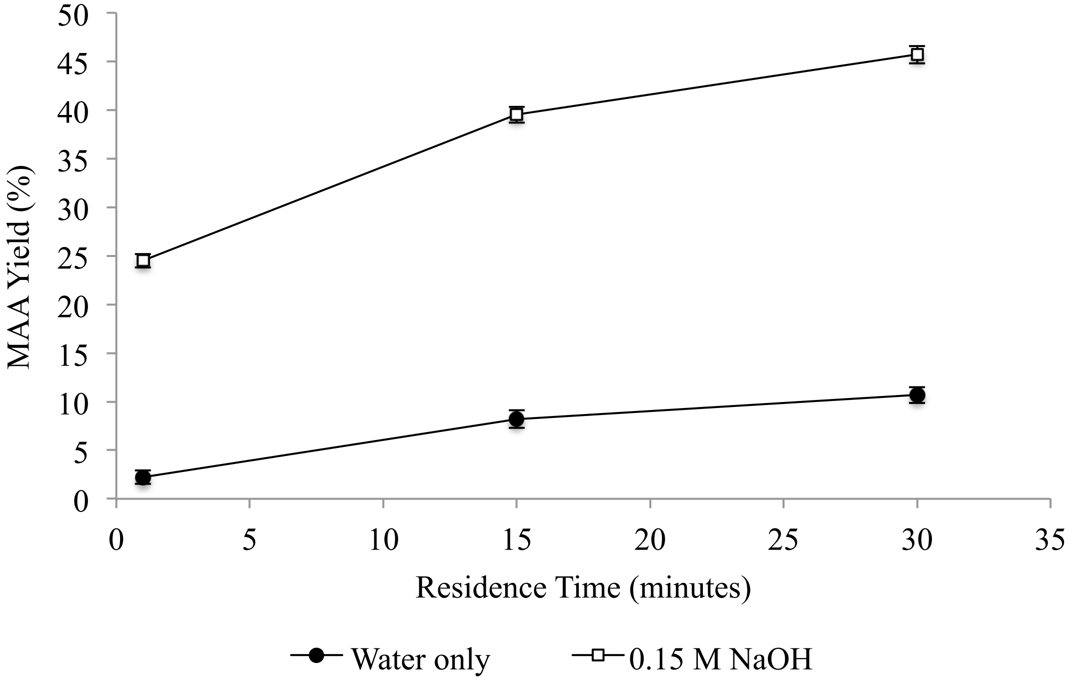


Figure 5.19: A comparison between methacrylic acid yield in blank reactions with and without NaOH (250 °C, 0.15 M NaOH, 20 g L^{-1} itaconic acid)

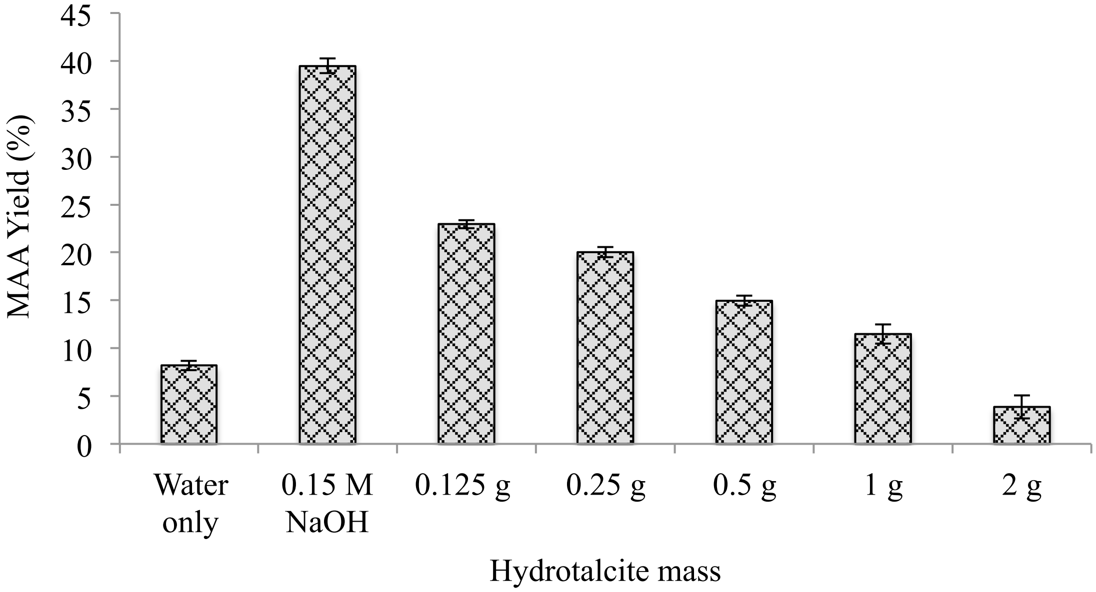


Figure 5.20: MAA yield at 250 °C, HTC calcined at 400 °C, Substrate: 20 g L^{-1} itaconic acid, Residence Time: 15 min

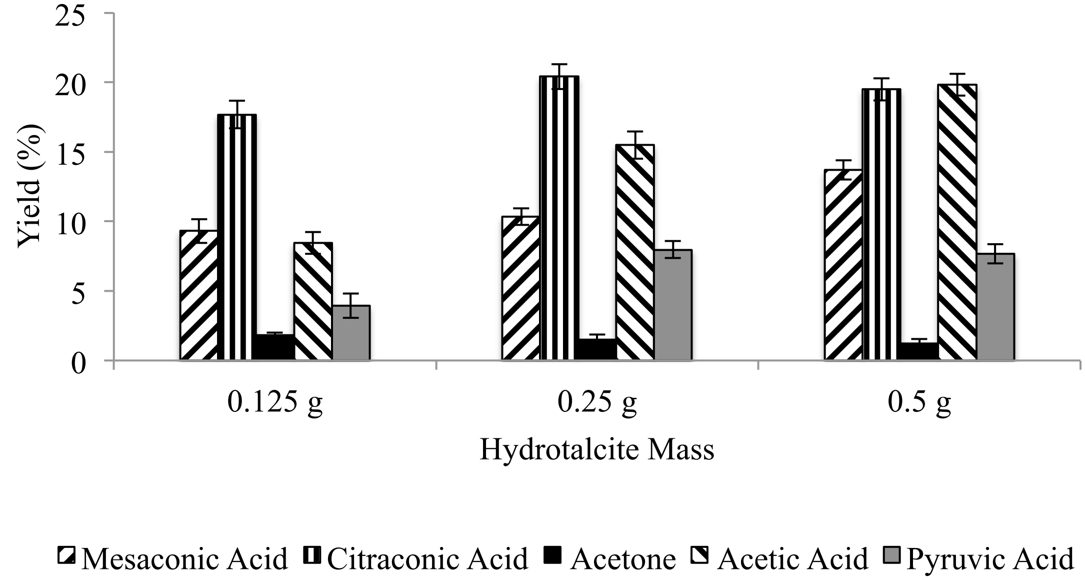


Figure 5.21: Byproduct yields at different hydrotalcite (calcined at 400 °C) masses (20 g L^{-1} itaconic acid, 1 min and 250 °C)

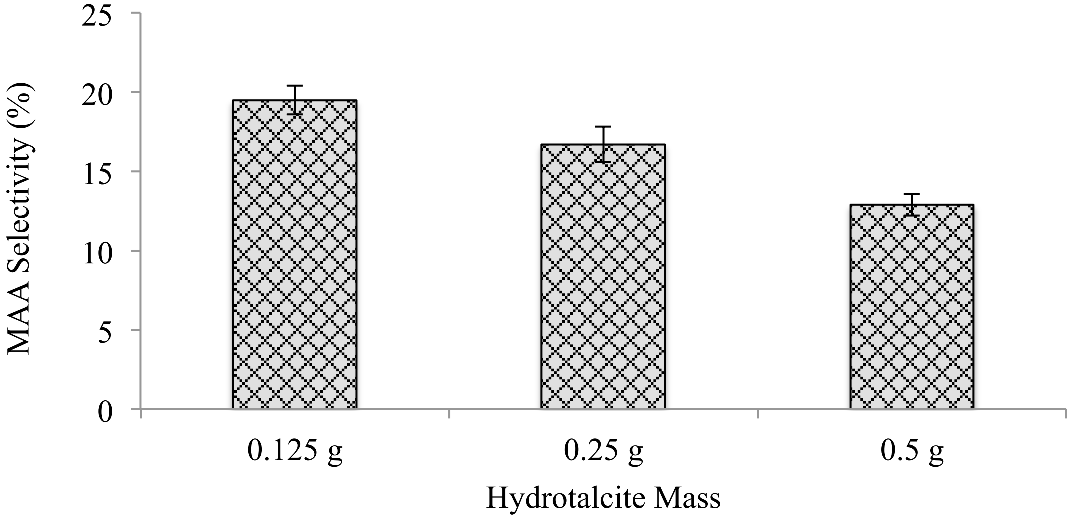


Figure 5.22: MAA selectivity at 250 °C (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} itaconic acid, 1 min)

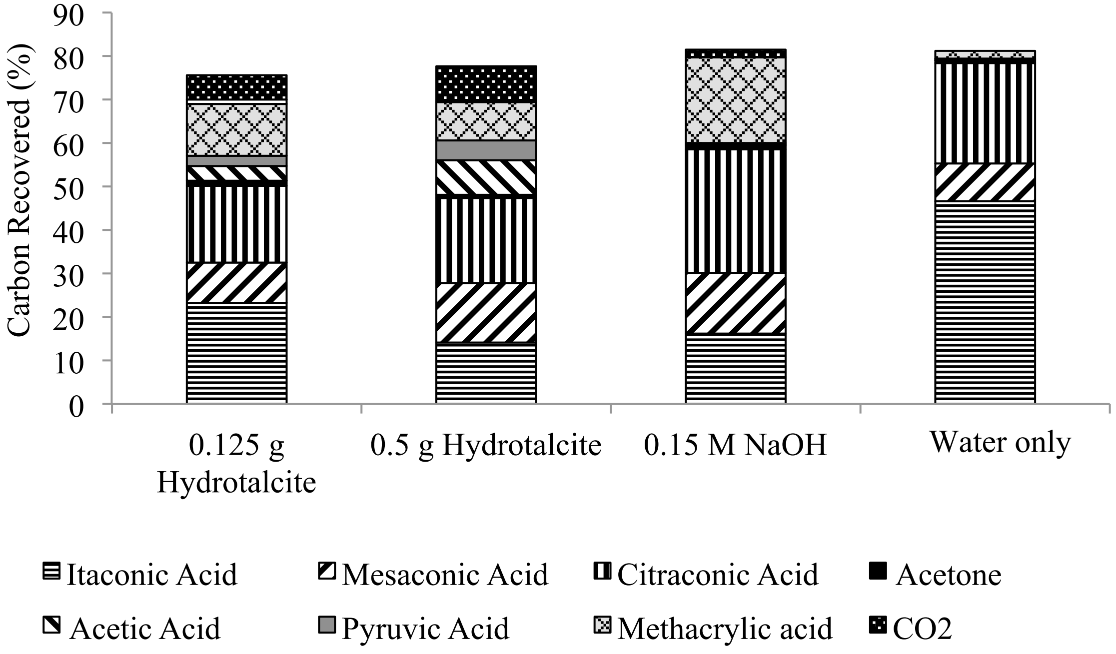


Figure 5.23: Carbon balance for itaconic acid reactions (reaction condition: 250 °C, 1 min, 20 g L^{-1} itaconic acid)

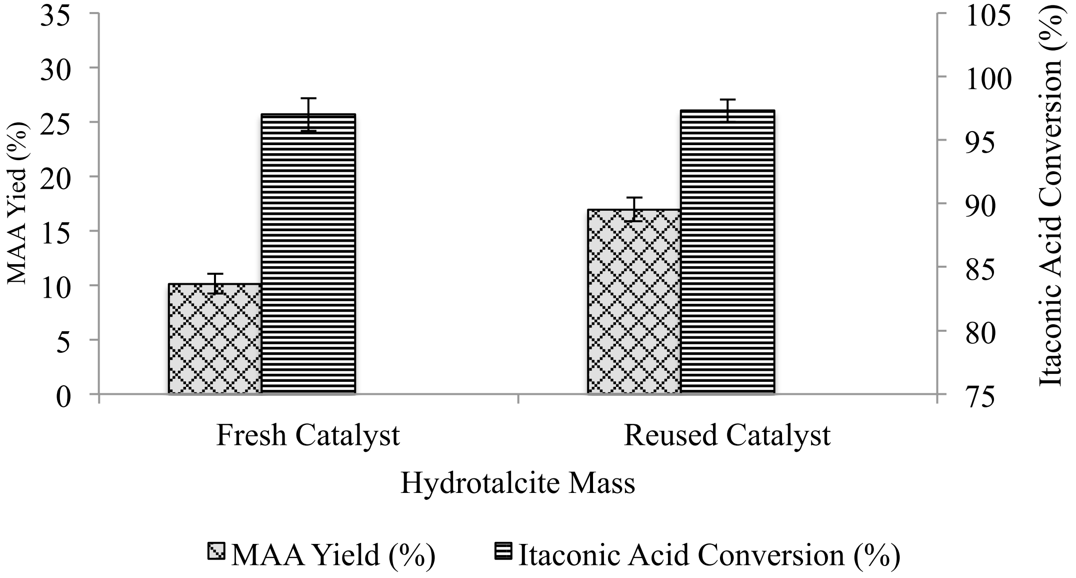


Figure 5.24: Effect of adding reused hydrotalcite on MAA yield (1 gram fresh hydrotalcite, 0.92 gram recovered hydrotalcite, 250 °C, 20 gL^{-1} itaconic acid, 5 minutes)

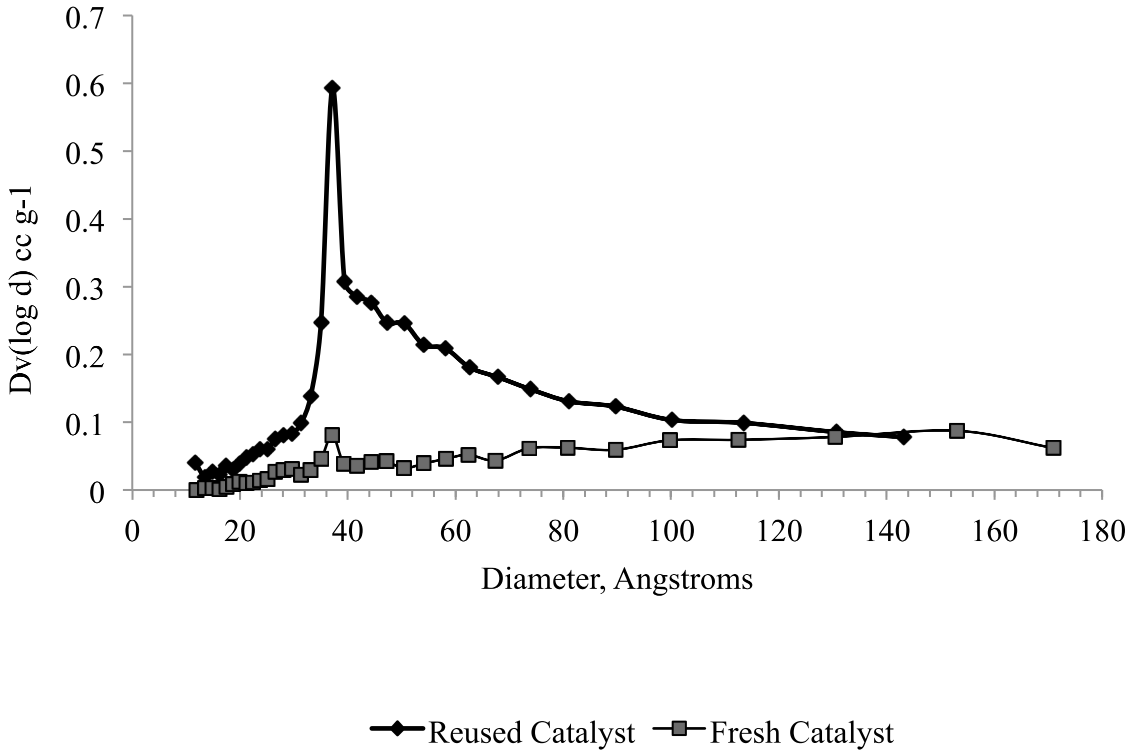


Figure 5.25: Pore size distribution for fresh and reused hydrotalcite. (Condition: 0.92 gram recovered hydrotalcite, 250 °C, 20 gL^{-1} itaconic acid, 5 minutes)

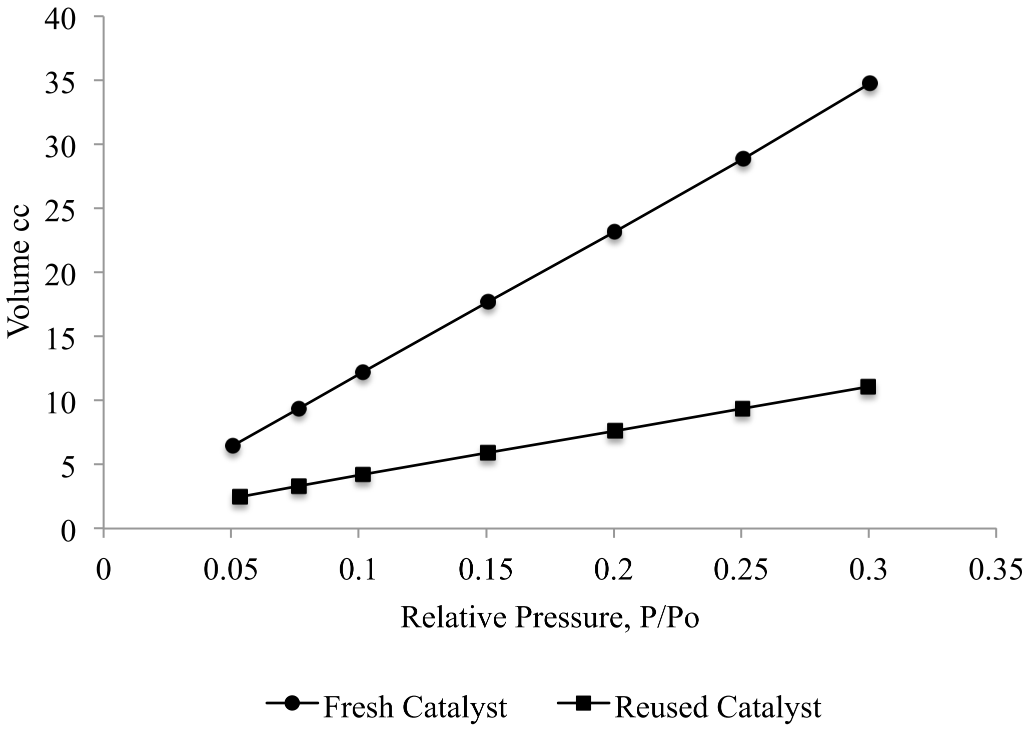


Figure 5.26: BET points for fresh and reused hydrotalcite. (Condition: 0.92 gram recovered hydrotalcite, 250 °C, 20 gL^{-1} itaconic acid, 5 minutes)

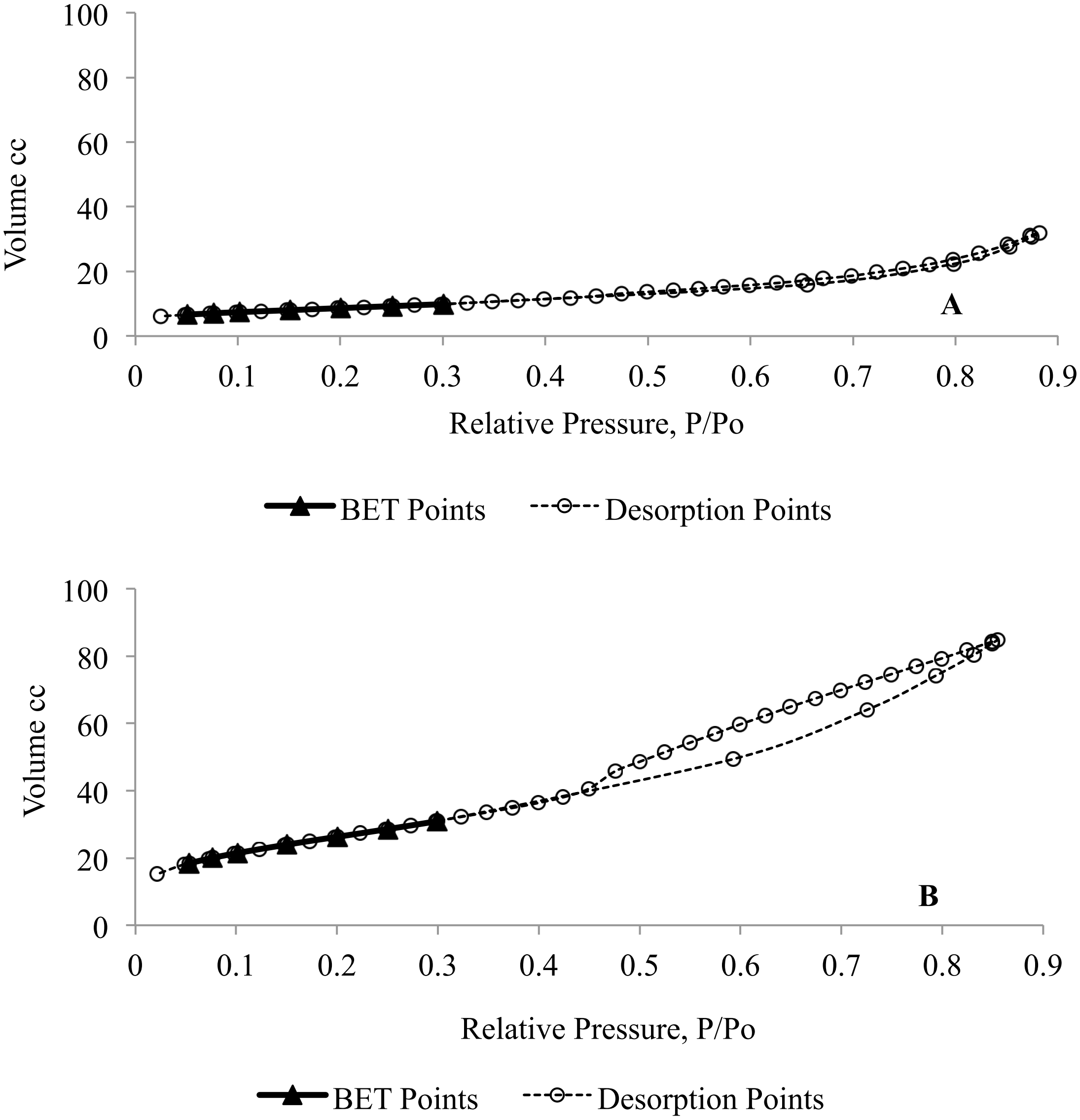


Figure 5.27: Isotherms for fresh (A) and reused hydrotalcite (B). (Condition: 0.92 gram recovered hydrotalcite, 250 °C, 20 gL^{-1} itaconic acid, 5 minutes)

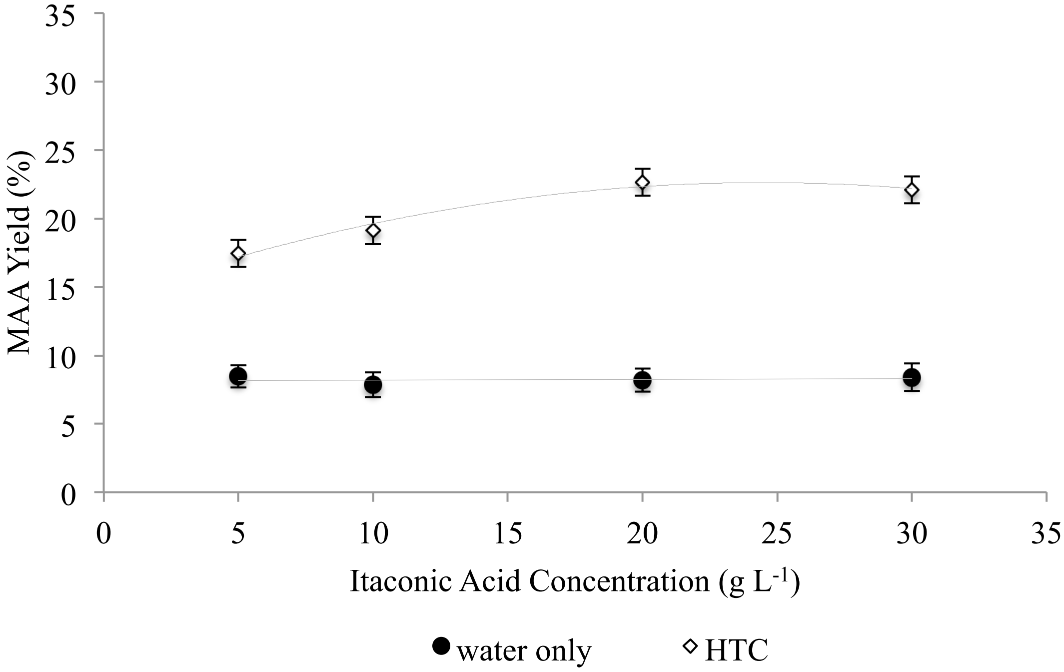


Figure 5.28: Effect of starting itaconic acid concentration on MAA yield (0.125 g HTC calcined at 400 °C, 15 minutes, 250 °C)

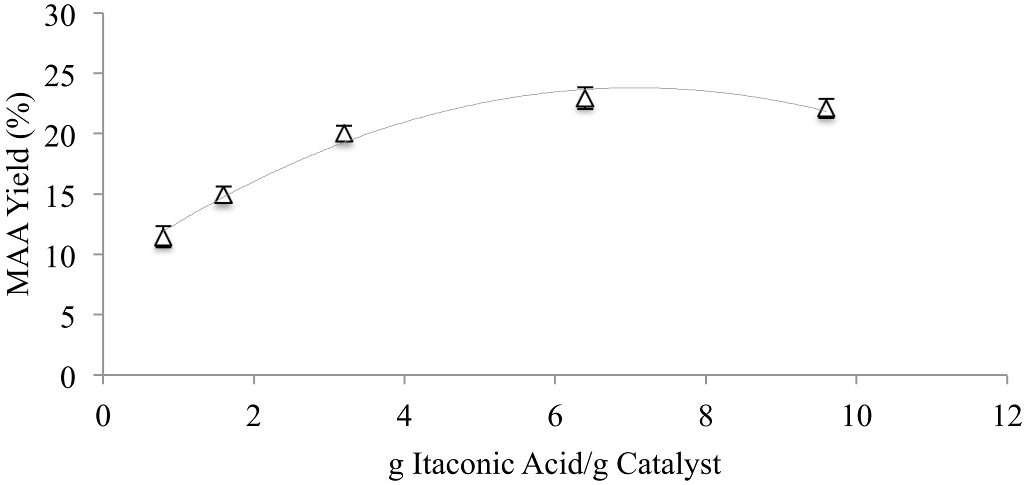


Figure 5.29: Optimum g itaconic acid/g hydrotalcite ratio (Condition: 250 °C, 15 minutes, hydrotalcite calcined 400 °C)

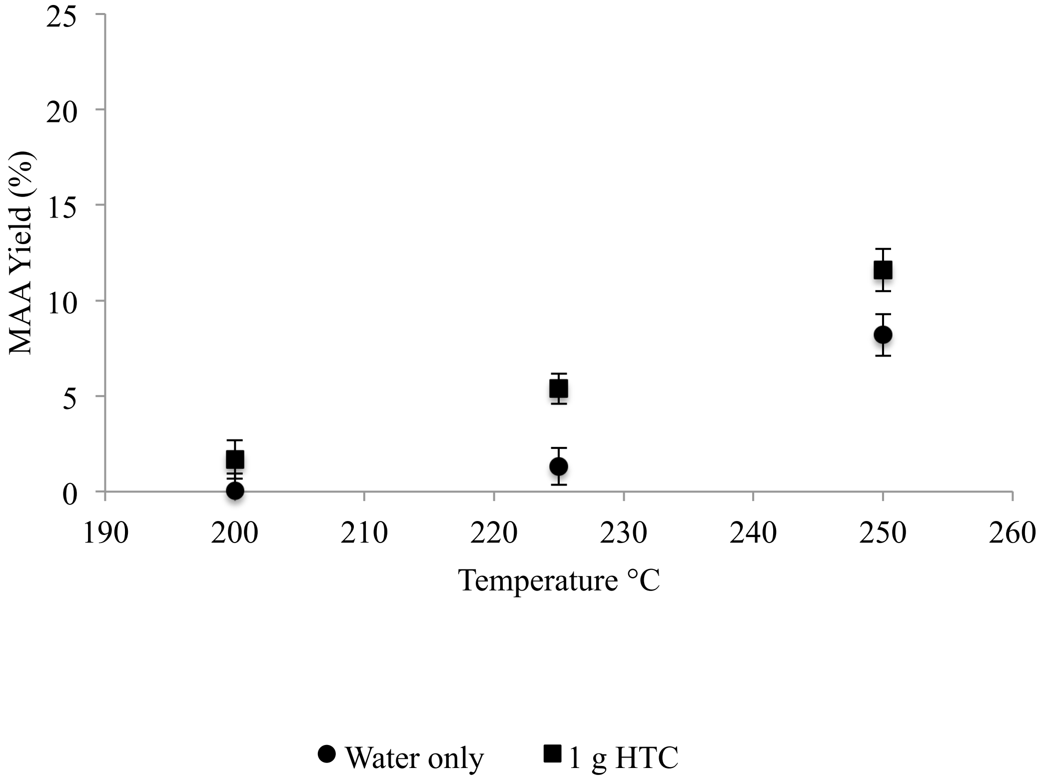


Figure 5.30: Effect of reaction temperature on methacrylic acid yield (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} itaconic acid, 15 min)

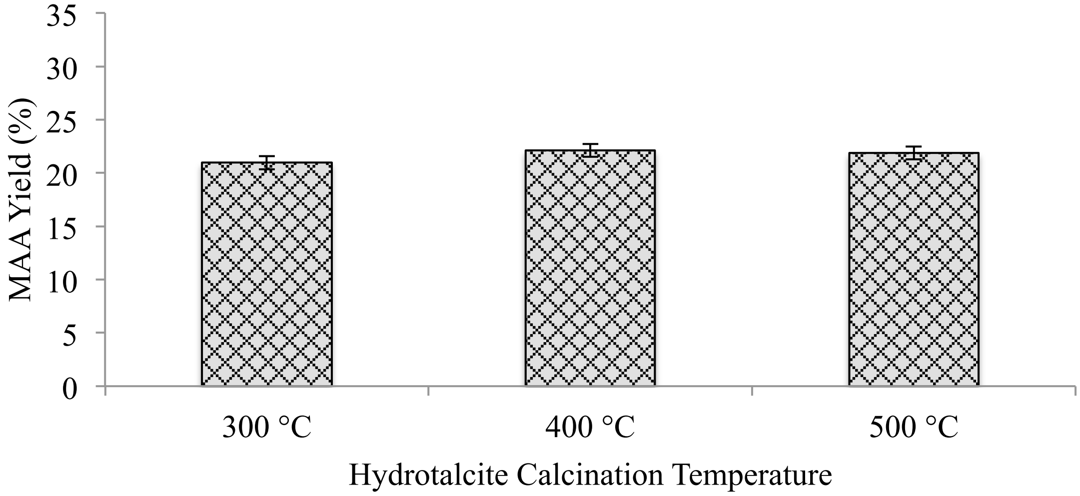


Figure 5.31: Effect of hydrotalcite calcination temperature on methacrylic acid yield (Substrate: 20 g L^{-1} itaconic acid, Residence Time: 15 min, Catalyst Amount: 0.125 g)

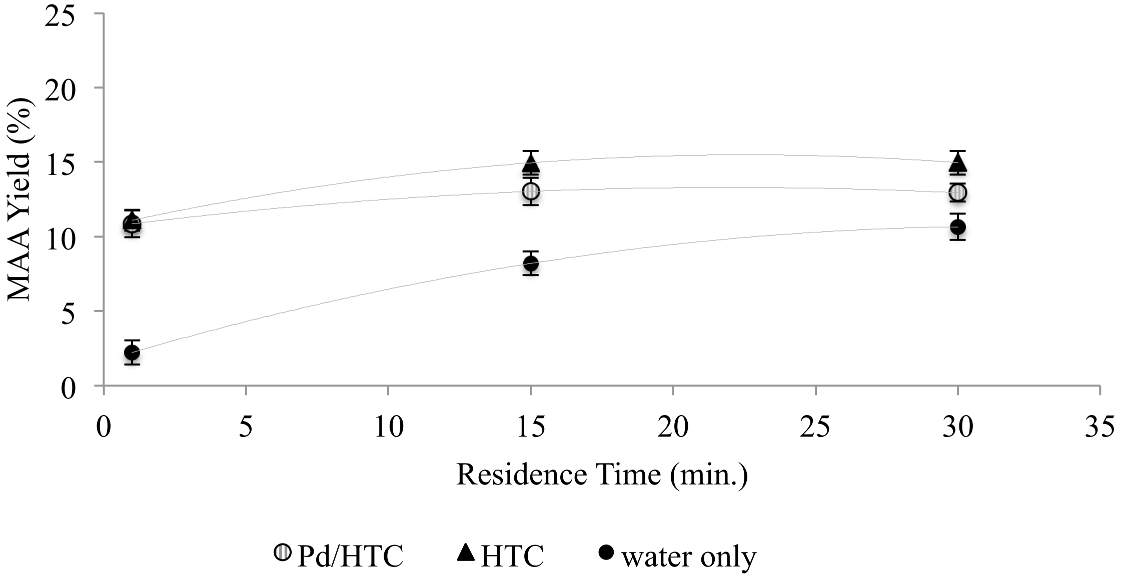


Figure 5.32: MAA yield versus residence time for palladium/hydrotalcite (Pd/C) and hydrotalcite (HTC calcined 400 °C) and blank reactions (Substrate: 20 g L^{-1} itaconic acid, Catalyst Amount: 0.5 g, Temperature: 250 °C)

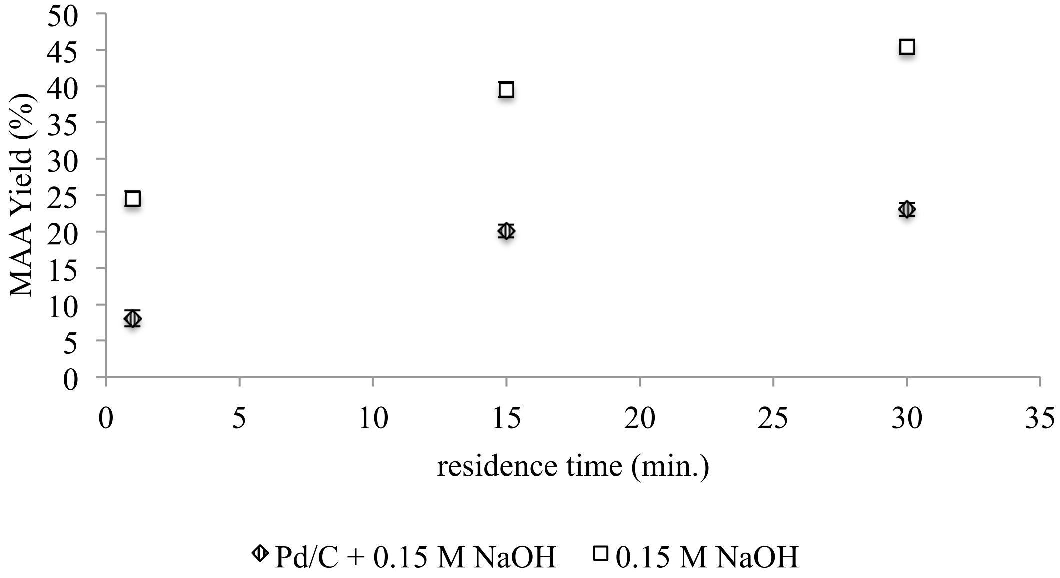


Figure 5.33: Effect of adding Palladium on carbon (Pd/C) to reaction media in presence of 0.15 M NaOH (Substrate: 20 g L^{-1} itaconic acid, Pd/ C mass: 1 g, Temperature: 250 °C)

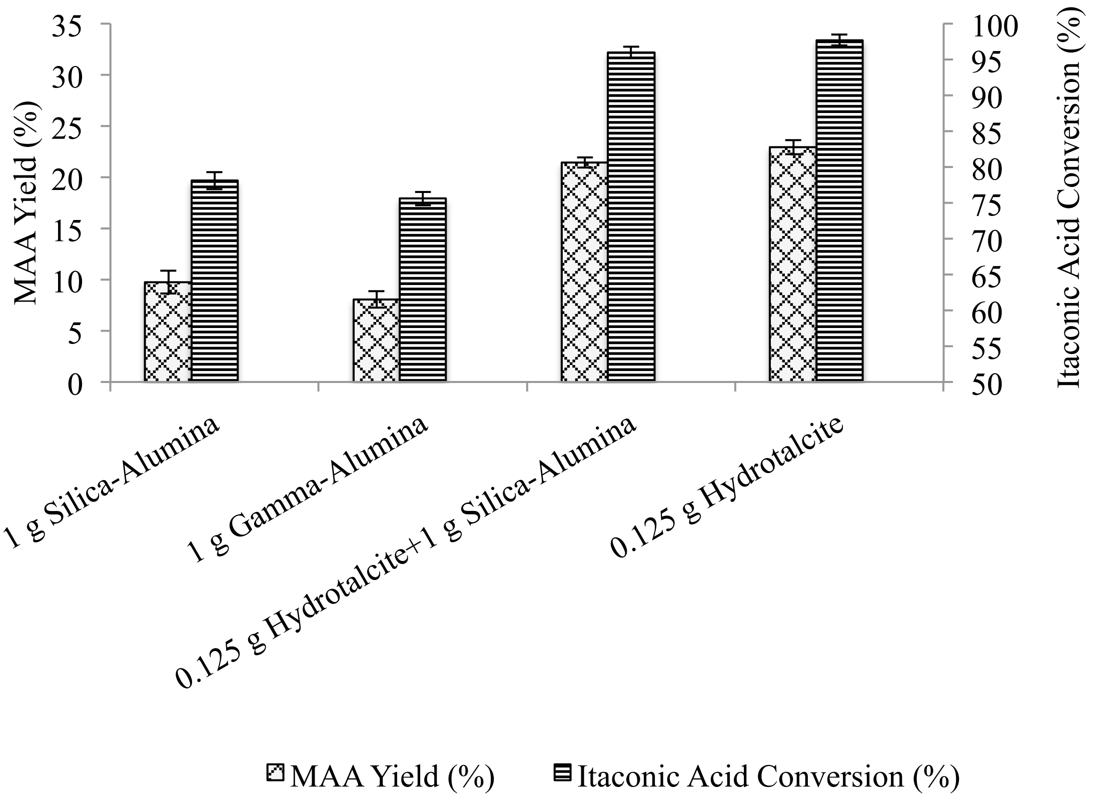


Figure 5.34: Effect of using acid catalyst on MAA yield (250 °C, Substrate: 20 g L^{-1} itaconic acid, Residence Time: 15 min- hydrotalcite was calcined at 400 °C)

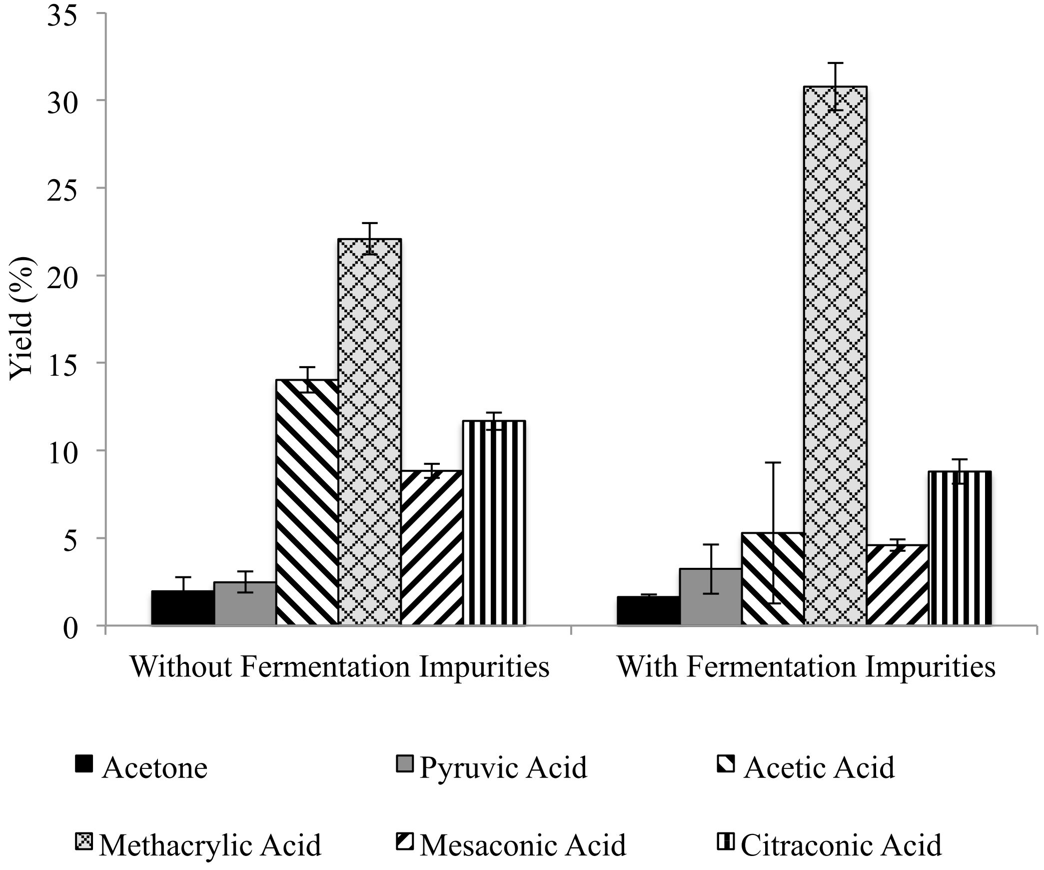


Figure 5.35: Effect of fermentation medium residuals on methacrylic acid and byproducts yield (Condition: 250 °C, Substrate: 30 g L^{-1} itaconic acid, Residence Time: 15 min- 0.125 g hydrotalcite calcined at 400 °C)

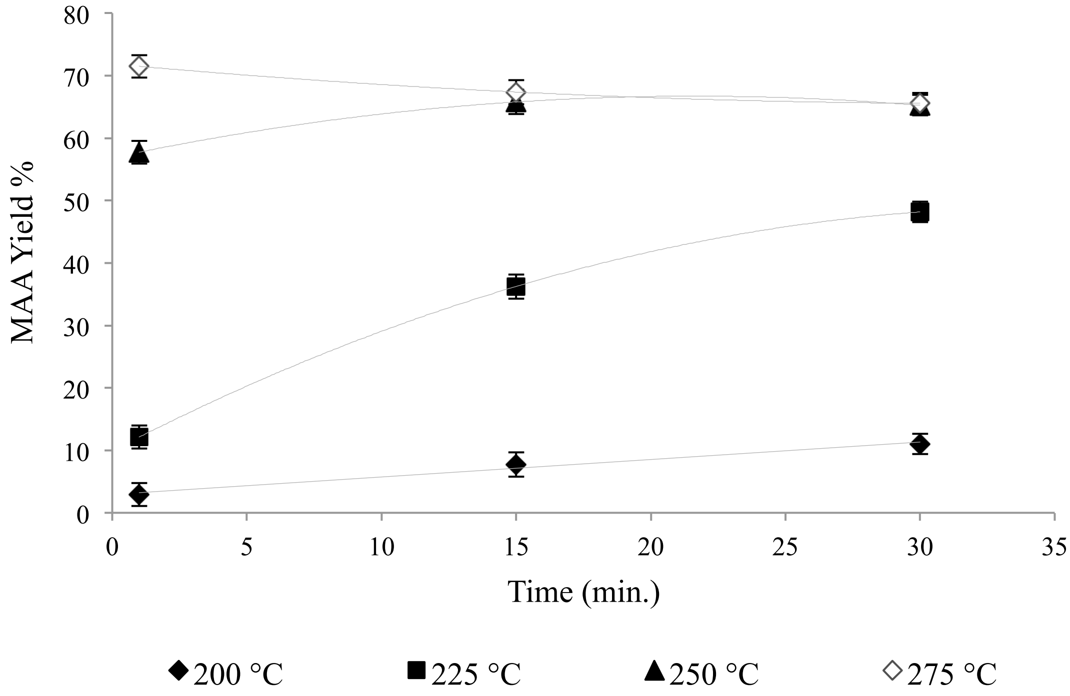


Figure 5.36: Methacrylic acid yield versus residence time at temperatures of 200 °C to 275 °C (Substrate: 20 g L^{-1} 2HIB acid)

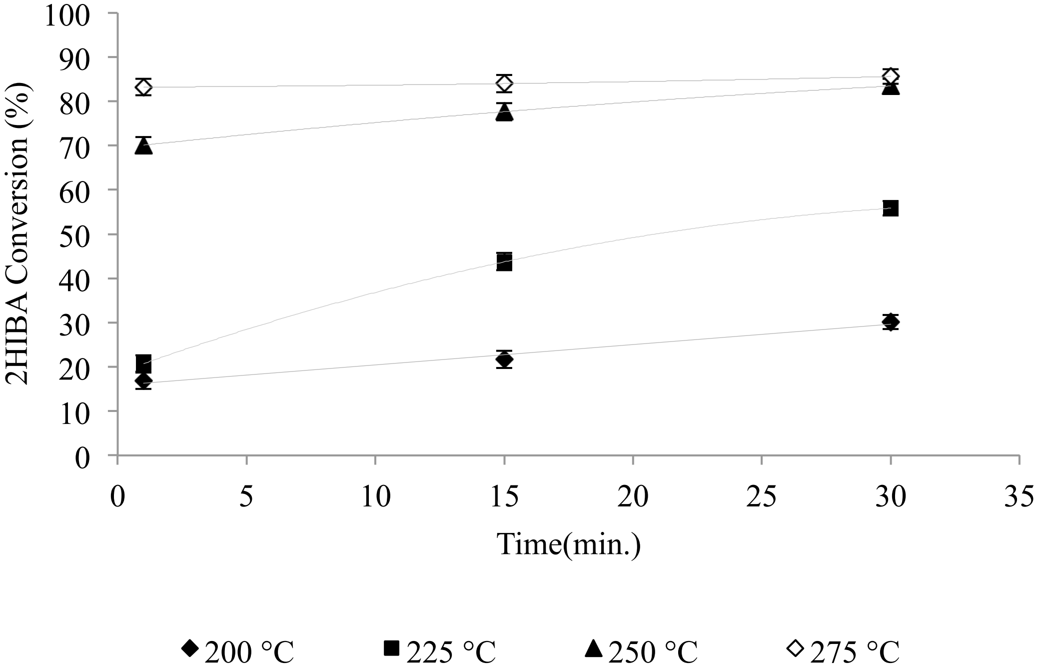


Figure 5.37: 2HIBA conversion vs. residence time at temperatures of 200 °C to 275 °C (Substrate: 20 g L^{-1} 2HIB acid)

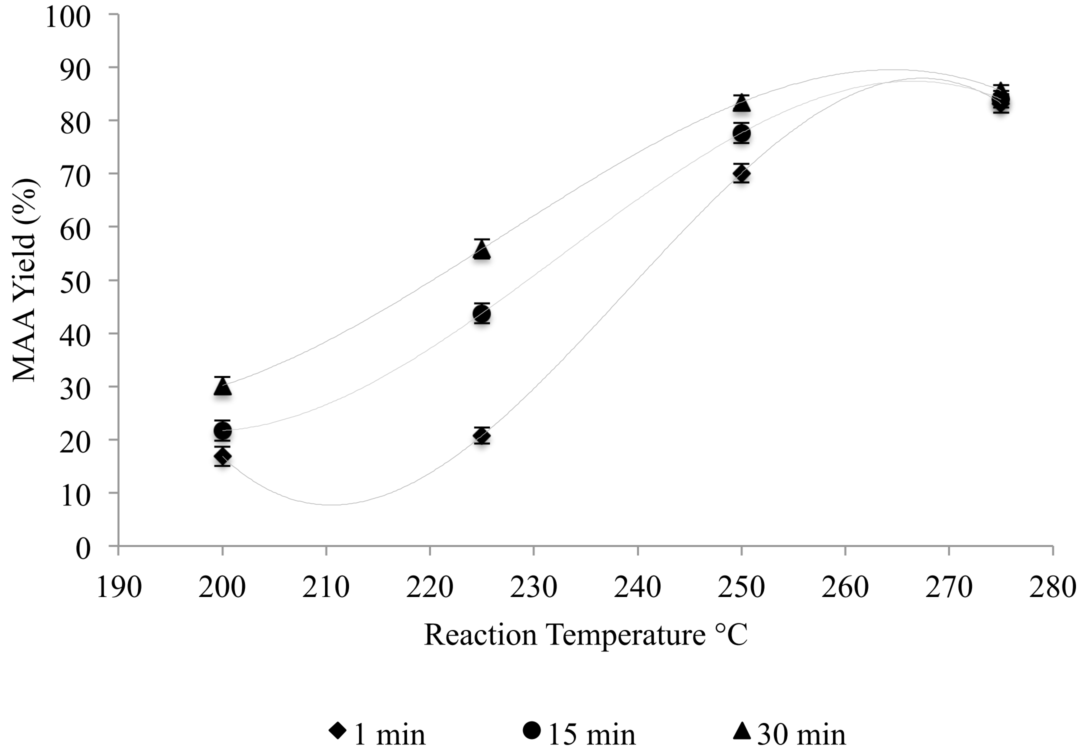


Figure 5.38: Effect of temperature on MAA yield, Substrate: 20 g L^{-1} 2HIB acid

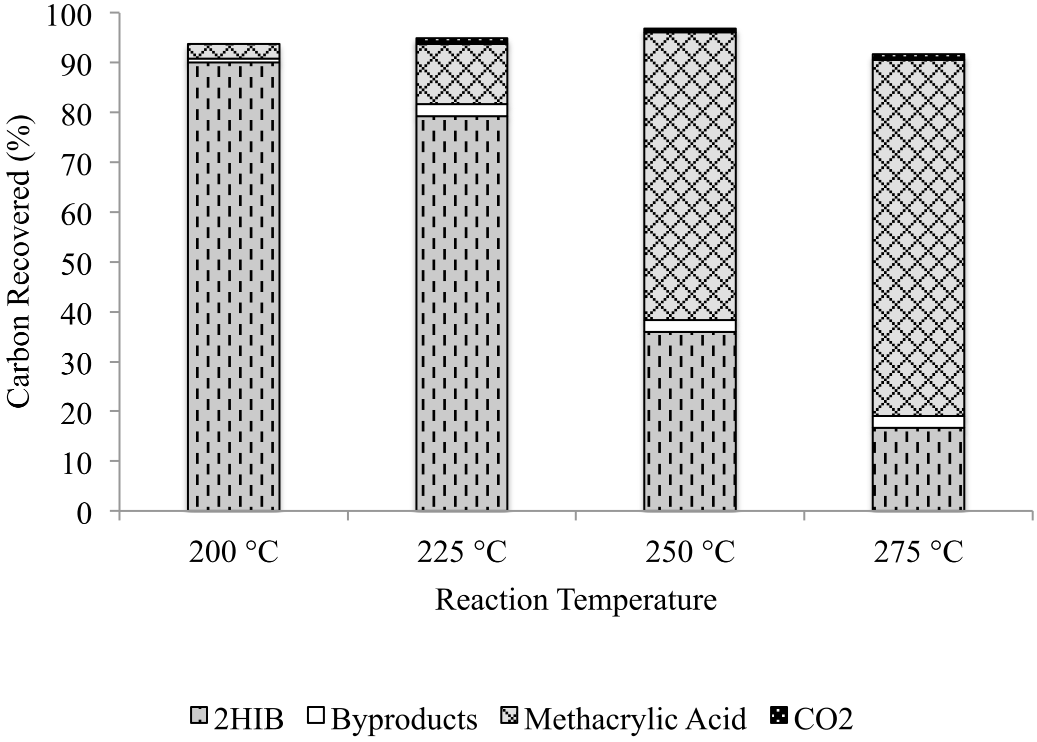


Figure 5.39: Carbon balance for 2-hydroxyisobutyric acid (2HIB) reactions (reaction condition: 1 min, 20 g L^{-1} 2HIB)

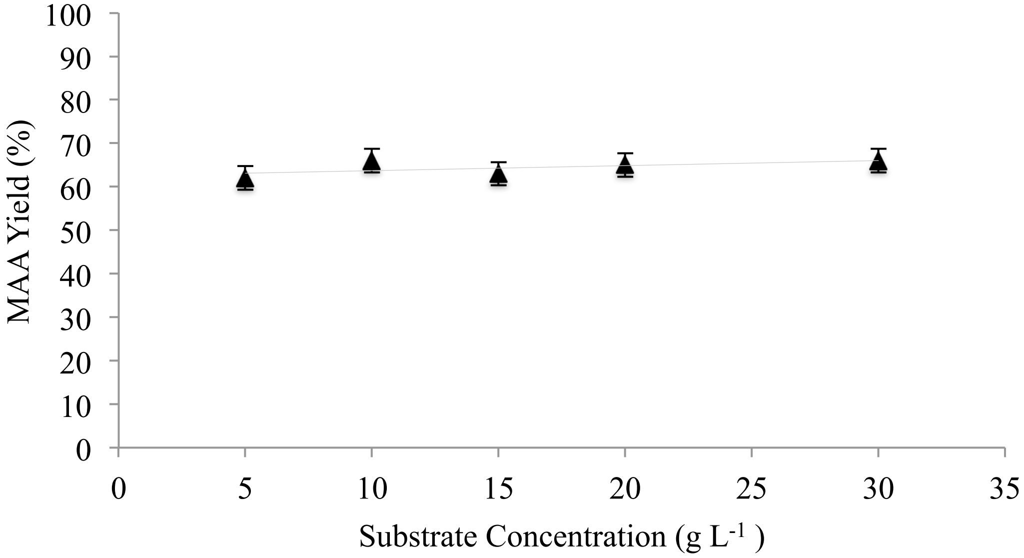


Figure 5.40: Effect of 2-hydroxyisobutyric acid concentration on MAA yield (15 minutes- 250 °C)

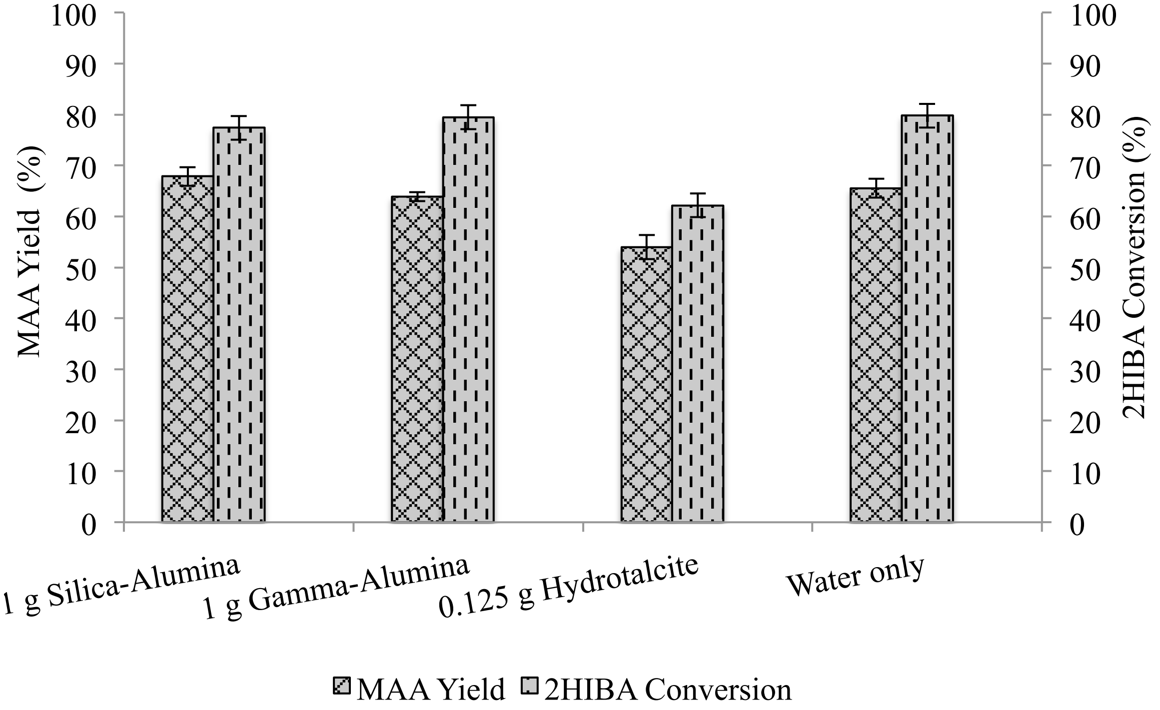


Figure 5.41: Effect of using acid catalyst on MAA yield (250 °C, Substrate: 20 g L^{-1} 2HIB acid, Residence Time: 15 min- hydrotalcite was calcined at 400 °C)

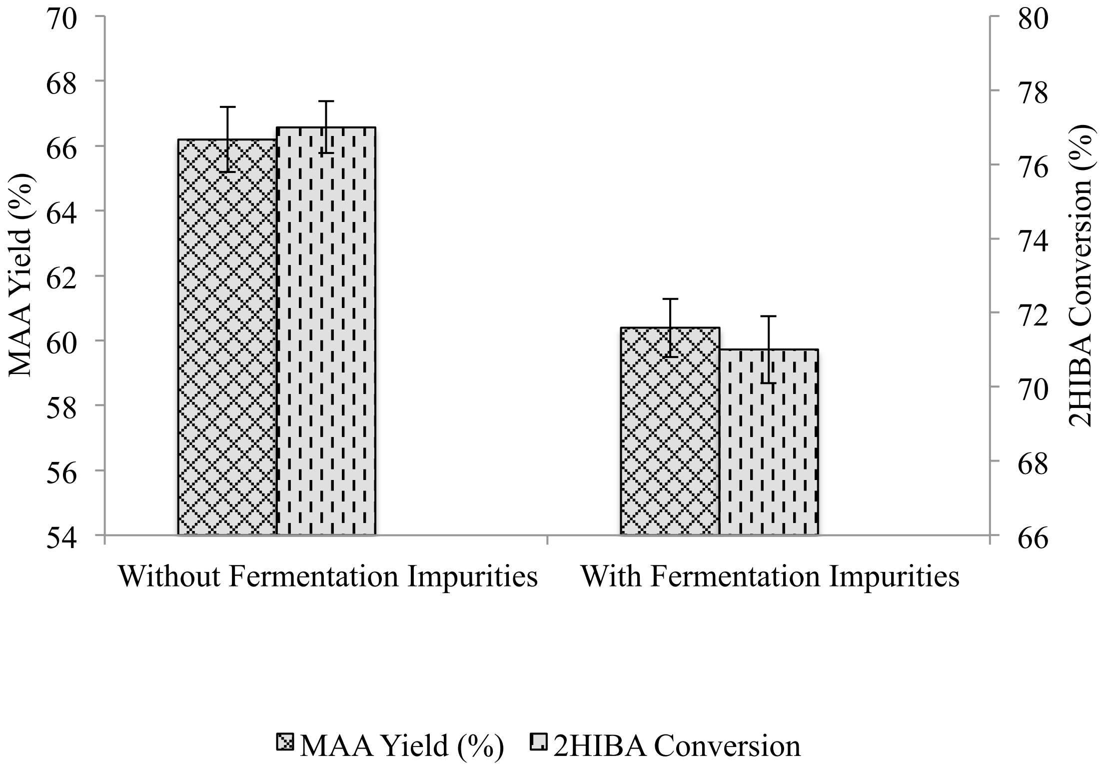


Figure 5.42: Effect of fermentation media residuals on methacrylic acid yield (Condition: 250 °C, Substrate: 30 g L^{-1} 2HIB acid, Residence Time: 15 min)

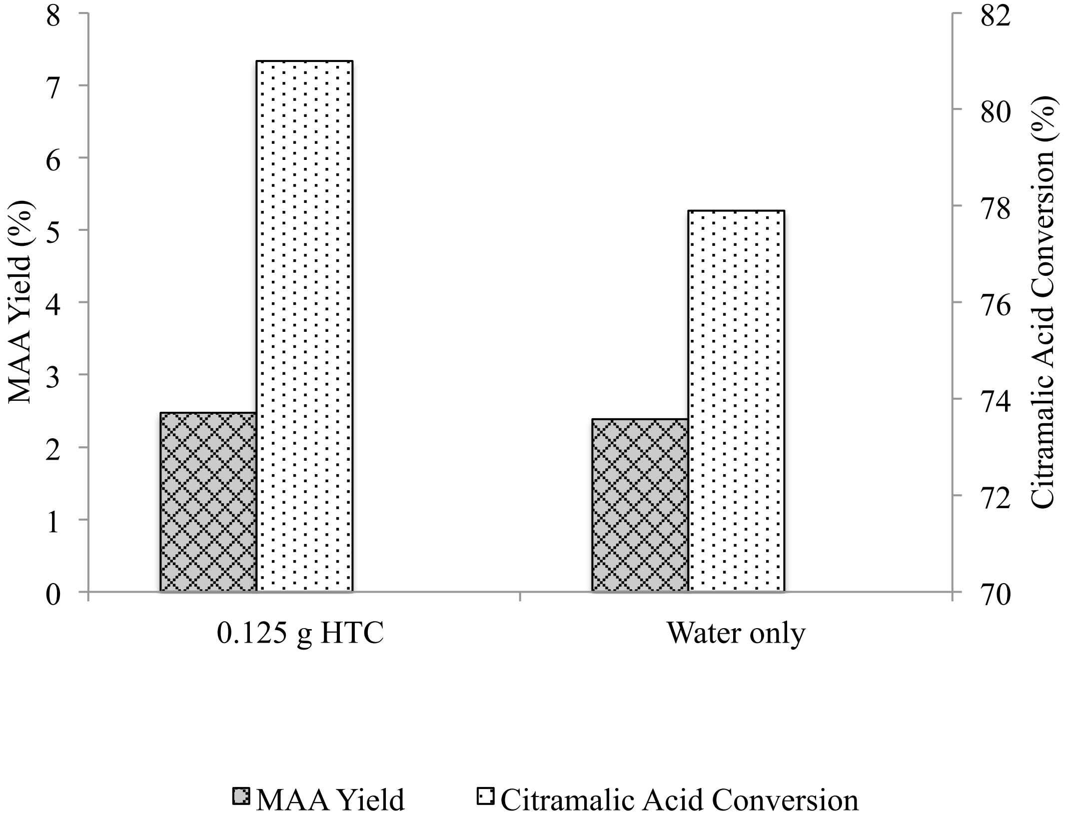


Figure 5.43: MAA yields and citramalic acid conversion at 250 °C (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} citramalic acid, 15 min)

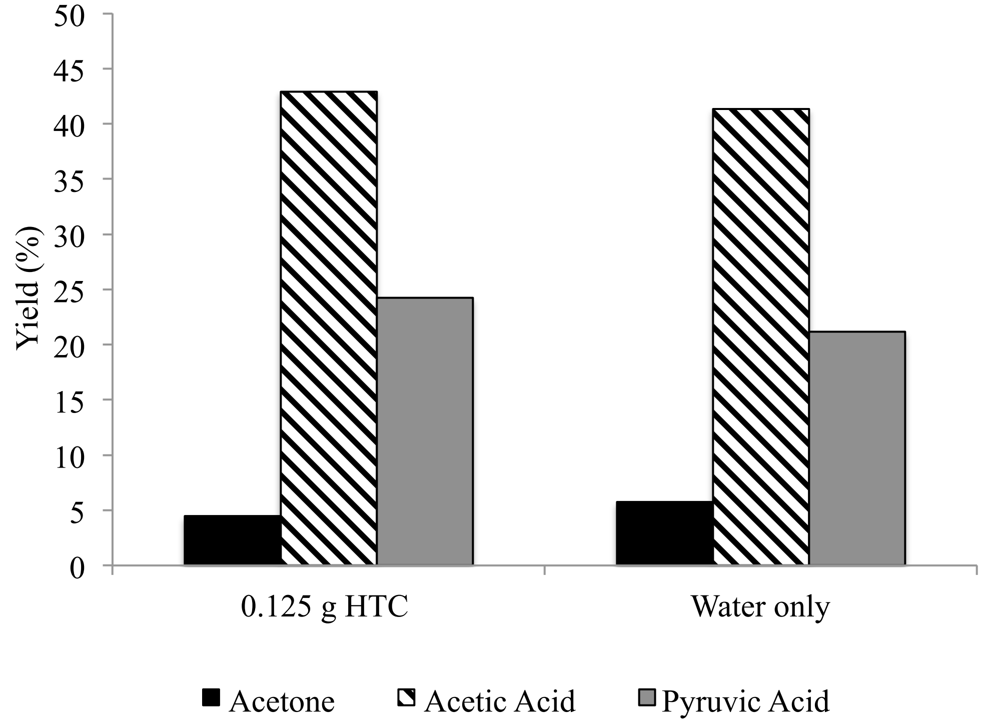


Figure 5.44: By-product yields at 250 °C (Hydrotalcite calcined at 400 °C, Substrate: 20 g L^{-1} citramalic acid, 15 min)

Table 5.1: Catalyst characterization for fresh and reused hydrotalcite (Reuse condition: 0.7/1 g HTC-250 °C, 20 g L^{-1} citric acid, 15 minutes)

Catalyst (Hydrotalcite)	**Surface Area (m^2 g^{-1})**	**Avg. Pore Size (Diameter, Å)**	**Total Pore Volume (cm^3 g^{-1})**
Fresh	30.71	12.45	0.00955
One-Step Reused	75.46	10.83	0.0204

Table 5.2: Catalyst characterization for fresh, reacted and reused hydrotalcite **(**Reuse condition: 0.92/1 g HTC-250 °C, 20 g L^{-1} itaconic acid, 5 minutes)

Catalyst (Hydrotalcite)	**Surface Area (m^2 g^{-1})**	**Avg. Pore Size (Diameter, Å)**	**Total Pore Volume (cm^3 g^{-1})**
Fresh	30.71	12.45	0.00955
Reacted	17.58	8.5	0.0037
One-Step Reused	98	9.6	0.0235

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