

Highly Efficient and Atom Economic Route for the Production of Methyl Acrylate and Acetic Acid from a Biorefinery Side Stream

Fatima El Ouahabi, Mykola Polyakov, Gerard P. M. van Klink, Sebastian Wohlrab, Sergey Tin, and Johannes G. de Vries*



Cite This: *ACS Sustainable Chem. Eng.* 2020, 8, 1705–1708



Read Online

ACCESS |



Metrics & More

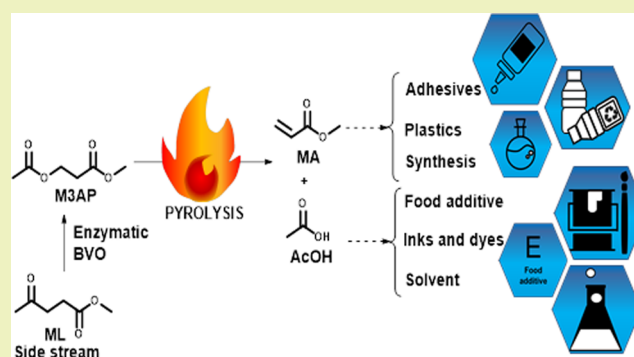


Article Recommendations



Supporting Information

ABSTRACT: We report a highly efficient and 100% atom economic synthesis of methyl acrylate and acetic acid via gas phase pyrolysis of methyl 3-acetoxypropionate at 600 °C. The latter can be produced in a single step from methyl levulinate, a side product of Avantium's FDCA process.



KEYWORDS: Renewable, Biorefinery, Gas phase elimination, Methyl levulinate, Methyl acrylate

INTRODUCTION

Fossil resources are limited, and therefore, renewable routes toward industrially relevant chemicals will be vital in the future.^{1–7} Methyl acrylate (MA) is a high volume monomer for the production of polymers.⁸ These polymers find application in many fields such as paints, coatings, adhesives, binders, etc. The petrochemical route toward this molecule uses propene as the starting material. However, in the past, acetylene has been used, and currently, many groups work on the conversion of propane.⁹

Several methods for the preparation of MA from renewable resources have been reported.¹⁰ For example, glycerol can be converted to acrolein,^{11–13} which is then reacted with methanol in the presence of an oxidant to afford the desired compound.¹⁴ MA can be directly prepared from 3-hydroxypropionic acid, obtained by fermentation, and methanol.¹⁵ Alternatively, 3-hydroxypropionic acid can be dehydrated to acrylic acid (AA) first,^{15–17} which can then be esterified to MA. Methyl lactate can be converted to MA, although here the hydroxy group has to be transformed into a leaving group in a separate step.^{18,19} Another route toward renewable MA is the condensation of methyl acetate with formaldehyde.^{20–22} In fact, acetic acid itself can be converted to AA via reaction with formaldehyde,²³ which can be esterified to MA. None of these processes have thus far been implemented on a large scale.

FDCA (2,5-furandicarboxylic acid) is a platform chemical, with great potential for the preparation of renewable plastics.²⁴ In particular, its polymer with ethylene glycol, polyethylene furandioate (PEF), has been touted as a renewable

replacement for polyethylene terephthalate (PET).²⁵ Although it can be prepared via oxidation of 5-HMF, this route has significant drawbacks. The stability of 5-HMF is rather low; therefore, the current preparation procedures from sugars result in poor isolated yields.^{26,27} In addition, it has a low shelf life. Under acidic conditions HMF undergoes polymerization to an insoluble material called humins.²⁸

The technology developed by Avantium offers an alternative route toward FDCA. In their process, the biobased sugars are first converted to 5-methoxymethyl-furfural (MMF), which is much more stable (Figure 1).²⁹ MMF is then oxidized to FDCA.³⁰ Since the reaction is performed in methanol, methyl levulinate (ML) is formed as a side product. Once FDCA is produced on a large scale (a 10 kTon plant is scheduled to open in 2023), an outlet needs to be found for this side product. Although many transformations of methyl levulinate are known, few of these lead to products for which a large market exists, with the possible exception of γ -valerolactone,³¹ and thus, there is a need for further conversions into useful existing products. In this paper, we show how ML can be converted into methyl acrylate via a high-yielding gas phase pyrolysis reaction of methyl 3-acetoxypropionate, which itself can be obtained in high yield via Bayer–Villiger oxidation of

Received: October 18, 2019

Revised: December 5, 2019

Published: January 13, 2020

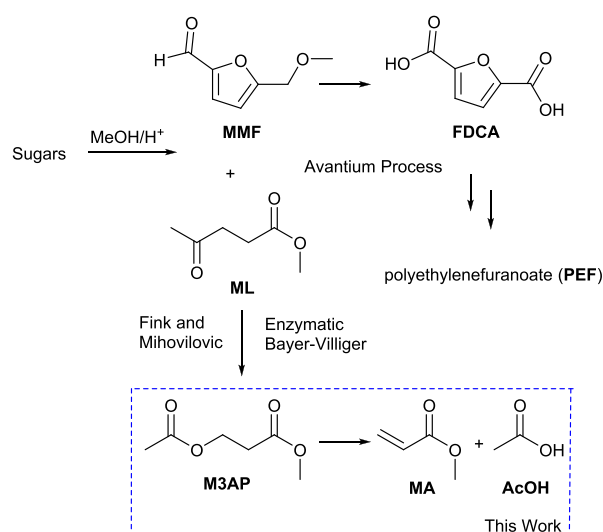


Figure 1. Methyl acrylate and acetic acid from biobased methyl levulinate.

methyl levulinate as published by others (*vide infra*) (Figure 1).

RESULTS AND DISCUSSION

Although the Baeyer–Villiger oxidation of benzyl levulinate was reported to proceed in 60% isolated yield,³² we just obtained mixtures of compounds in the attempted BV reaction of methyl levulinate with H₂O₂ catalyzed by acids. Indeed, Mascari has reported that the BV reaction of levulinic acid gives mixtures of succinic acid and 2-hydroxypropionic acid, but the latter underwent a retro-aldol reaction to ultimately form acetic acid and formaldehyde.³³ Fortunately, a good enzymatic procedure was recently reported by Fink and Mihovilovic, who performed the conversion of ML to methyl 3-acetoxypropionate (M3AP) in 80% yield using a Baeyer–Villiger monoxygenase.³⁴ Since this procedure uses oxygen rather than hydrogen peroxide as oxidant, it is clear that this is scalable chemistry.

With the route from ML to M3AP secured, we decided to explore the catalytic elimination of acetic acid from M3AP.

The reactions were performed by flowing gasified M3AP (diluted with nitrogen) through a tube filled with a catalyst at various temperatures in the gas phase. The results are shown in

Table 1. Amberlyst 15 afforded higher activity than the palladium catalyst at 300 °C (Table 1, entries 1 and 2), although its selectivity was very poor. Trying to improve the efficiency of the reaction with the palladium catalyst, the temperature was increased to 400 °C. The selectivity toward MA remained above 80%, although the selectivity toward acetic acid was reduced to 69%. In all these reactions, one of the side products found was methyl acetate, which presumably is the result of an acid-catalyzed transesterification between acetic acid and either methyl acrylate or M3AP. Also, acetic acid is known to undergo decarboxylation in the presence of palladium catalysts at these temperatures.³⁵ The latter explains the lower selectivity toward AcOH compared to MA. A further increase in temperature results in a large drop of the selectivity of the reaction (54% to MA and 39% to AcOH, Table 1, entry 4).

Since the catalytic experiments appeared to be unselective due to the side reactions, we decided to investigate an uncatalyzed gas-phase elimination of acetic acid from M3AP. The pyrolysis of alkyl acetates is known to yield an alkene obtaining acetic acid as a side product. This reaction proceeds through a thermal *syn* elimination in which the carbonyl group of the acetate assists in abstraction of the proton (Figure 2).³⁶

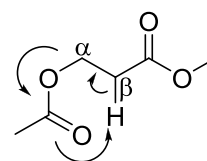


Figure 2. Mechanism of the acetate pyrolysis *via* β-elimination.

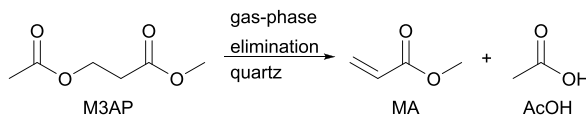
Taylor reported the effect of the β-alkoxycarbonyl group in the pyrolysis of 3-acetoxypropionates. In that kinetic investigation, it was found that the rate of the pyrolysis of methyl acetoxypropionate is 100 times higher than that of the pyrolysis of ethyl-acetoxypropionate at 600 K.³⁷ The author claims that the β-MeO₂C group therefore activates the elimination by enhancing the acidity of the β-hydrogen.

We have performed the pyrolysis of M3AP in a quartz tube filled with quartz pieces. The results are shown in Table 2. The reaction does not work at 400 °C or lower temperatures (Table 2, entries 1 and 2). Only partial conversion was detected at 500 or 550 °C (Table 2, entries 3 and 4). At 600

Table 1. Catalytic Gas-Phase Elimination of Acetic Acid from Methyl 3-Acetoxypropanoate

Entry ^a	Catalyst	T (°C)	Conversion of M3AP (%)	Yield of MA (%)	Yield of AcOH (%)	MB ^b (%)
1	Amberlyst 15	300	47	13	15	70
2	1 wt % Pd/Al ₂ O ₃	300	24	20	19	98
3	1 wt % Pd/Al ₂ O ₃	400	49	40	31	91
4	1 wt % Pd/Al ₂ O ₃	500	89	48	35	58

^aGeneral conditions: continuous flow of gas-phase M3AP (0.5 mL h⁻¹, 3.8 mmol h⁻¹) and N₂ gas (20 mL min⁻¹) through a tube filled with a 1 cm³ bed volume (200 mg) of the corresponding catalyst at the reaction temperature. Total flow, 1.3 L/h; M3AP:N₂ molar ratio, 1:13; GHSV, 1284 h⁻¹; contact time, 3 s. The resulting conversions and yields were calculated by GC using dimethylformamide (DMF) as the external standard. ^bMB = mass balance.

Table 2. Nuncatalytic Gas-Phase Elimination of Acetic Acid from Methyl 3-Acetoxypropionate


Entry ^a	T (°C)	Conversion of M3AP (%)	Yield of MA (%)	Yield of AcOH (%)
1	300	0	—	—
2	400	0	—	—
3	500	49	46	46
4 ^b	550	58	57	54
5 ^b	600	99	98	97

^aGeneral conditions: continuous flow of gas-phase M3AP (0.5 mL h⁻¹, 3.8 mmol h⁻¹) and N₂ gas (20 mL min⁻¹) through a quartz tube filled with 7 cm³ quartz pieces at the reaction temperature. Total flow, 1.3 L h⁻¹; M3AP:N₂ molar ratio, 1:13; GHSV, 183 h⁻¹; contact time, 20 s. The resulting conversions and yields were calculated by GC and ¹H NMR. ^bAverage of two experiments.

°C, 99% of M3AP was converted, resulting in the formation of MA in 98% yield. On top of that, the yield of acetic acid is also almost quantitative (97%) under the reaction conditions. It is also worth mentioning that in all these reactions the analyses have shown no other side products. The two products are easily separable by distillation.¹⁸

CONCLUSION

In conclusion, we found that gas-phase pyrolysis of methyl 3-acetoxypropionate results in almost quantitative yields of methyl acrylate (98%) and acetic acid (97%). In contrast to the unselective catalytic reactions, no other side products were detected by GC analysis. This allows the simultaneous production of these two industrially important molecules via a two-step process starting from methyl levulinate. Although the reaction temperature may seem high, this is not really a problem on large scale as the heat produced in the reaction can be used to form high temperature steam, which is the universal energy carrier used on almost all large chemical sites.

Hence, this is a green and 100% atom efficient way to utilize this side stream compound to useful chemicals. In addition, once levulinic acid is produced on a large scale from lignocellulosic biomass, it will also be possible to produce methyl acrylate at a price which is competitive with its current fossil price.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06215>.

General considerations, description of the pyrolysis setup, general procedure for the pyrolysis of M3AP, general procedure for the catalytic elimination of acetic acid from M3AP, GC analyses of the catalytic and pyrolysis reactions, and references (PDF)

AUTHOR INFORMATION

Corresponding Author

Johannes G. de Vries – Leibniz Institut für Katalyse e. V. an der Universität Rostock, Rostock 18059, Germany;

orcid.org/0000-0001-5245-7748;
Email: johannes.devries@katalyse.de

Authors

Fatima El Ouahabi – Leibniz Institut für Katalyse e. V. an der Universität Rostock, Rostock 18059, Germany

Mykola Polyakov – Leibniz Institut für Katalyse e. V. an der Universität Rostock, Rostock 18059, Germany

Gerard P. M. van Klink – Avantium Chemicals B.V., Amsterdam 1014 BV, The Netherlands

Sebastian Wohlrab – Leibniz Institut für Katalyse e. V. an der Universität Rostock, Rostock 18059, Germany; orcid.org/0000-0003-1407-7263

Sergey Tin – Leibniz Institut für Katalyse e. V. an der Universität Rostock, Rostock 18059, Germany

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acssuschemeng.9b06215>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the European Union for funding this project, which was part of the Marie Skłodowska-Curie ITN-EID “HUGS” program (H2020_MSCA-ITN-2015-675325).

ABBREVIATIONS

ML, methyl levulinate; FDCA, 2,5-furandicarboxylic acid; HMF, 5-hydroxymethyl-furfural; MMF, 5-methoxymethyl-furfural; M3AP, methyl 3-acetoxy-propionate; MA, methyl acrylate; AcOH, acetic acid; MB, mass balance

REFERENCES

- Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J., Jr.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The Path Forward for Biofuels and Biomaterials. *Science* **2006**, *311*, 484–489.
- Corma, A.; Iborra, S.; Velty, A. Chemical Routes for the Transformation of Biomass into Chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502.
- Vennestrøm, P. N. R.; Osmundsen, C. M.; Christensen, C. H.; Taarning, E. Beyond Petrochemicals: The Renewable Chemicals Industry. *Angew. Chem., Int. Ed.* **2011**, *50*, 10502–10509.
- Tuck, C. O.; Pérez, E.; Horváth, I.; Sheldon, R. A.; Poliakoff, M. Valorization of Biomass: Deriving More Value from Waste. *Science* **2012**, *337*, 695–699.
- Delidovich, I.; Hausoul, P. J. C.; Deng, L.; Pfitzenreuter, R.; Rose, M.; Palkovits, R. Alternative Monomers Based on Lignocellulose and Their Use for Polymer Production. *Chem. Rev.* **2016**, *116*, 1540–1599.
- Deuss, P. J.; Barta, K.; de Vries, J. G. Homogeneous Catalysis for the Conversion of Biomass and Biomass-derived Platform Chemicals. *Catal. Sci. Technol.* **2014**, *4*, 1174–1196.
- Stadler, B. M.; Wulf, C.; Werner, T.; Tin, S.; de Vries, J. G. Catalytic Approaches to Monomers for Polymers Based on Renewables. *ACS Catal.* **2019**, *9*, 8012–8067.
- Bauer, W., Jr. Acrylic Acid and Derivatives. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley-VCH: Hoboken, NJ, 2003. DOI: 10.1021/acscatal.9b01665.
- Ohara, T.; Sato, T.; Shimizu, N.; Prescher, G.; Schwind, H.; Weiberg, O.; Marten, K.; Greim, H. Acrylic Acid and Derivatives. In *Ullmann's Encyclopedia of Industrial Chemistry*; John Wiley & Sons: Berlin, 2011; p 1–18. DOI: 10.1002/14356007.a01_161.pub3.

- (10) Makshina, E. V.; Canadell, J.; van Krieken, J.; Peeters, E.; Dusselier, M.; Sels, B. F. Bio-Acrylates Production: Recent Catalytic Advances and Perspectives of the Use of Lactic Acid and Their Derivates. *ChemCatChem* **2019**, *11*, 180–201.
- (11) Sarkar, B.; Pendem, C.; Sivakumar Konathala, L. N.; Tiwari, R.; Sasaki, T.; Bal, R. Cu Nanoclusters Supported on Nanocrystalline SiO₂-MnO₂: a Bifunctional Catalyst for the One-step Conversion of Glycerol to Acrylic Acid. *Chem. Commun.* **2014**, *50*, 9707–9710.
- (12) Craciun, L.; Benn, G.; Dewing, J.; Schriver, G.; Peer, W.; Siebenhaar, B.; Siegrist, U. *Catalyst for Preparing Acrolein or Acrylic Acid by Dehydration Reaction of Glycerin and Method for Producing the Same*. US Patent US20110112330A1, 2011.
- (13) Jiang, X. C.; Zhou, C. H.; Tesser, R.; Di Serio, M.; Tong, D. S.; Zhang, J. R. Coking of Catalysts in Catalytic Glycerol Dehydration to Acrolein. *Ind. Eng. Chem. Res.* **2018**, *57*, 10736–10753.
- (14) Dey, S.; Gadakh, S. K.; Sudalai, A. Titanium Superoxide–a Stable Recyclable Heterogeneous Catalyst for Oxidative Esterification of Aldehydes with Alkylarenes or Alcohols Using TBHP as an Oxidant. *Org. Biomol. Chem.* **2015**, *13*, 10631–10640.
- (15) Craciun, L.; Benn, G.; Dewing, J.; Schriver, G.; Peer, W.; Siebenhaar, B.; Siegrist, U. *Preparation of Acrylic Acid Derivatives from Alpha-or Beta-Hydroxy Carboxylic Acids*. US Patent US20050222458A1, 2005.
- (16) Lilga, M.; White, J.; Holladay, J.; Zacher, A.; Muzatko, D.; Orth, R. US Patent *Method for Conversion of Beta-Hydroxy Carbonyl Compounds*. US20070219391A1, 2007.
- (17) Bogan, L. E.; Silvano, M. A.; Zolotorofe, D. L. *Process for Converting a Hydroxycarboxylic Acid, or Salts thereof, to an Unsaturated Carboxylic Acid and/or its Esters*. US Patent US20090076297A1, 2009.
- (18) Ratchford, W. P.; Fisher, C. H. Methyl Acrylate by Pyrolysis of Methyl Acetoxypropionate. *Ind. Eng. Chem.* **1945**, *37*, 382–387.
- (19) Godlewski, J. E.; Velásquez, J. E.; Collias, D. I. *Conversion of Methyl-2-Acetoxy Propionate to Methyl Acrylate and Acrylic Acid*. US Patent US20130296602A1, 2013.
- (20) Jiang, S.; Li, C.; Chen, H.; Yang, D.; Zhang, S. One-Step Synthesis of Methyl Acrylate Using Methyl Acetate with Formaldehyde in a Fluidized Bed Reactor. *Ind. Eng. Chem. Res.* **2017**, *56*, 9322–9330.
- (21) Bao, Q.; Bu, T.; Yan, J.; Zhang, C.; Ning, C.; Zhang, Y.; Hao, M.; Zhang, W.; Wang, Z. Synthesis of Methyl Acrylate by Aldol Condensation of Methyl Acetate with Formaldehyde Over Al₂O₃-Supported Barium Catalyst. *Catal. Lett.* **2017**, *147*, 1540–1550.
- (22) Zuo, C.; Li, C.; Ge, T.; Guo, X.; Zhang, S. Spherical P-Modified Catalysts for Heterogeneous Cross-aldol Condensation of Formaldehyde with Methyl Acetate for Methyl Acrylate Production. *Can. J. Chem. Eng.* **2017**, *95*, 2104–2111.
- (23) Parvulescu, A.-N.; Lange de Oliveira, A.; Lejkowski, M.; Woerz, N. T.; Hartmann, M.; Amakawa, K.; Goebel, M.; Mueller, U.; Feyen, M.; Liu, Y. *Process for Preparing Acrylic Acid Using an Aluminum-Free Zeolitic Material*. US Patent US20150343431A1, 2015.
- (24) Sajid, M.; Zhao, X.; Liu, D. Production of 2,5-Furandicarboxylic Acid (FDCA) from 5-Hydroxymethylfurfural (HMF): Recent Progress Focusing on the Chemical-Catalytic Routes. *Green Chem.* **2018**, *20*, 5427–5453.
- (25) de Jong, E.; Dam, M. A.; Sipos, L.; Gruter, G.-J. M. Furandicarboxylic Acid (FDCA), a Versatile Building Block for a Very Interesting Class of Polyesters. In *Biobased Monomers, Polymers, and Materials*; Smith, P. B., Gross, R. A., Eds.; ACS Symposium Series 1105; American Chemical Society: Washington, DC, 2012; p1–13. DOI: 10.1021/bk-2012-1105.ch001.
- (26) Galkin, K. I.; Krivodaeva, E. A.; Romashov, L. V.; Zalesskiy, S. S.; Kachala, V. V.; Burykina, J. V.; Ananikov, V. P. Critical Influence of 5-Hydroxymethylfurfural Aging and Decomposition on the Utility of Biomass Conversion in Organic Synthesis. *Angew. Chem., Int. Ed.* **2016**, *55*, 8338–8342.
- (27) Wozniak, B.; Tin, S.; de Vries, J. G. Bio-based building blocks from 5-hydroxymethylfurfural via 1-hydroxyhexane-2,5-dione as intermediate. *Chem. Sci.* **2019**, *10*, 6024–6034.
- (28) Patil, S. K. R.; Lund, C. R. F. Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural. *Energy Fuels* **2011**, *25*, 4745–4755.
- (29) De Sousa Dias, A. S. V.; Gruter, G.-J. M.; van Putten, R.-J. *Process for the Conversion of a Carbohydrate-Containing Feedstock*. WIPO Patent WO2012091570A1, 2012.
- (30) Muñoz de Diego, C.; Schammel, W. P.; Dam, M. A.; Gruter, G. J. M. *Method for the Preparation of 2,5-Furandicarboxylic Acid and Esters thereof*. WIPO Patent WO2011043660A2, 2011.
- (31) Filiciotto, L.; Balu, A. M.; Van der Waal, J. C.; Luque, R. Catalytic Insights into the Production of Biomass-Derived Side Products Methyl Levulinate, Furfural and Humins. *Catal. Today* **2018**, *302*, 2–15.
- (32) Cannon, J. G.; Garst, J. E. Preparation and Baeyer-Villiger Reaction of Certain 2-Carbalkoxycyclopropyl Methyl Ketones. *J. Pharm. Sci.* **1975**, *64*, 1059–1061.
- (33) Dutta, S.; Wu, L.; Mascal, M. Efficient, Metal-Free Production of Succinic Acid by Oxidation of Biomass-Derived Levulinic acid with Hydrogen Peroxide. *Green Chem.* **2015**, *17*, 2335–2338.
- (34) Fink, M. J.; Mihovilovic, M. D. Non-hazardous Baeyer-Villiger oxidation of Levulinic Acid Derivatives: Alternative Renewable Access to 3-Hydroxypropionates. *Chem. Commun.* **2015**, *51*, 2874–2877.
- (35) Contreras-Mora, J.; Banerjee, R.; Bolton, B.; Valentin, J.; Monnier, J. R.; Williams, C. T. Characterization and Evaluation of Carbon-Supported Noble Metals for the Hydrodeoxygenation of Acetic Acid. *Org. Process Res. Dev.* **2018**, *22*, 1628–1635.
- (36) de Burgh Norfolk, S.; Taylor, R. The mechanism of the gas-phase pyrolysis of esters. Part IV. Effects of substituents at the β -carbon atom. *J. Chem. Soc., Perkin Trans. 2* **1976**, 280–285.
- (37) Taylor, R. The mechanism of ester pyrolysis. Part 10. The effect of the β -methoxycarbonyl group in pyrolysis of methyl 3-acetoxypropionate. *J. Chem. Res., Synop.* **1981**, 250–251.