

From Glucose to Fuel: Converting Biomass into an Energy Source

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Introduction

Biomass is living or recently dead biological material that can be used as fuel. If biomass can be efficiently converted into high energy density fuel, it could become a renewable source of fuel and could replace some fuels derived from petroleum. According to a joint USDA/DOE study in 2006, over one billion tons of biomass can be produced annually in the US without affecting food, feed or fiber uses. In biomass, long polymers of sugars, such as glucose and arabinose, can be converted into a hydrocarbon, which can be burned as fuel. The first step of this conversion (Figure 1) is to break down the polymer into its sugar monomers. These sugars must be extended into a longer chain molecule and finally deoxygenated and hydrogenated to yield a hydrocarbon which can be burned identically to a petroleum derived hydrocarbon.

This project focuses on the carbon chain extension reactions of biomass derived sugars using water-based organometallic catalysis. High energy density fuels are between eight and fifteen carbons in length whereas biomass sugars are only five or six carbons. The carbon chain of these sugars must be extended in order for them to be burned as fuel. Additionally, our main goal is produce these molecules in an environmentally friendly reaction and to obtain commercially viable yields. Therefore, this project will focus on using an environmentally friendly solvent (i.e. water) and a low reaction temperature (> 100°C) to produce high yields of extended carbon chain molecules. The starting materials for these reactions are glucose and 5-hydroxymethylfurfural (HMF), a direct derivative of glucose. These molecules will undergo an aldol reaction using an organometallic catalyst to produce a molecule between nine and fifteen carbons in length. The starting materials and catalysts will be varied in order to determine which reactions produce the highest yields at the mildest reaction conditions. Ultimately, we would like to determine if any of these reactions could be used in a commercial process to convert biomass into high energy density fuel.

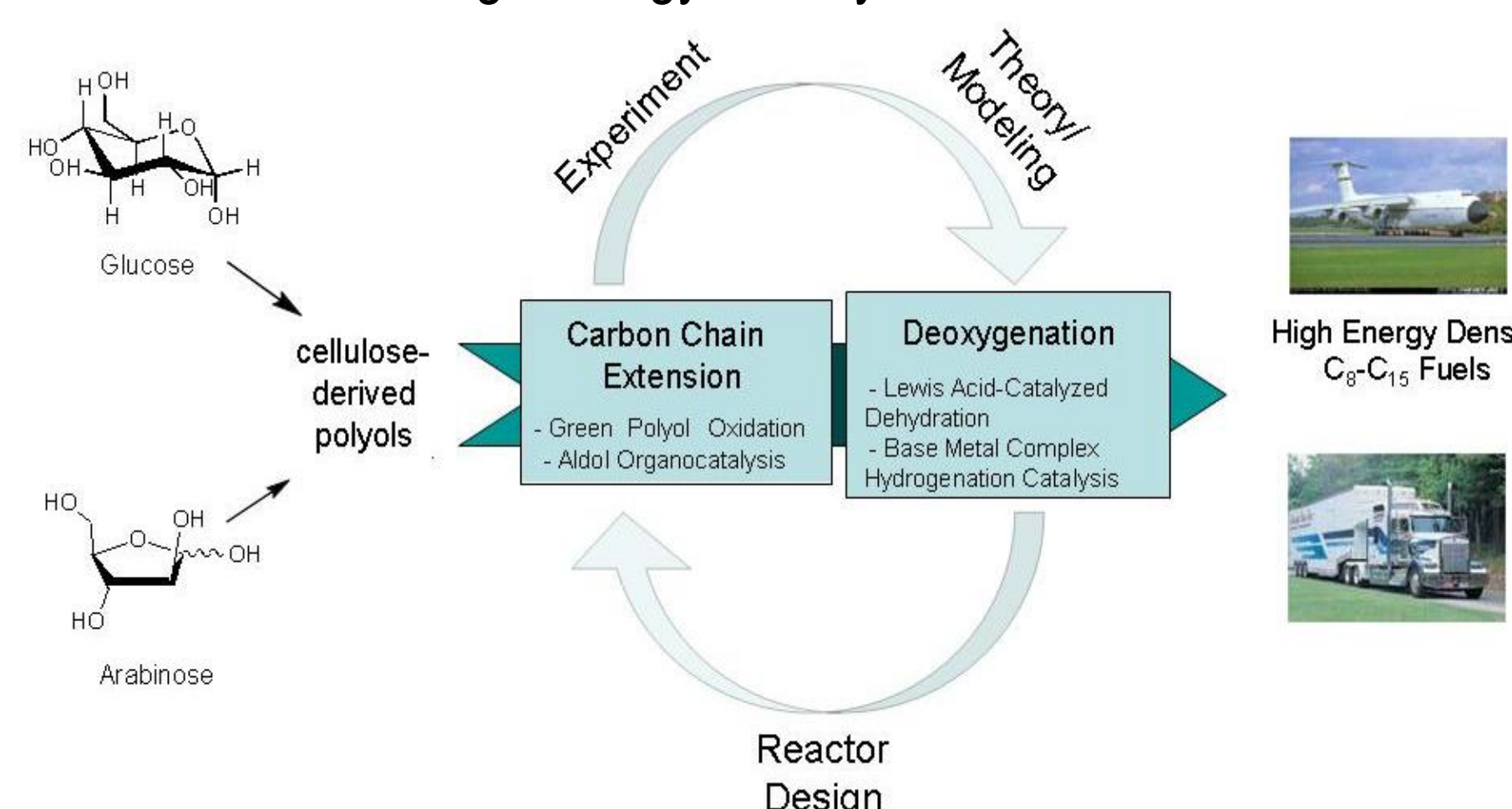


Figure 1. Process for converting biomass into high energy density fuel. This project focused on the carbon chain extension step of this process.

Aldol Reaction

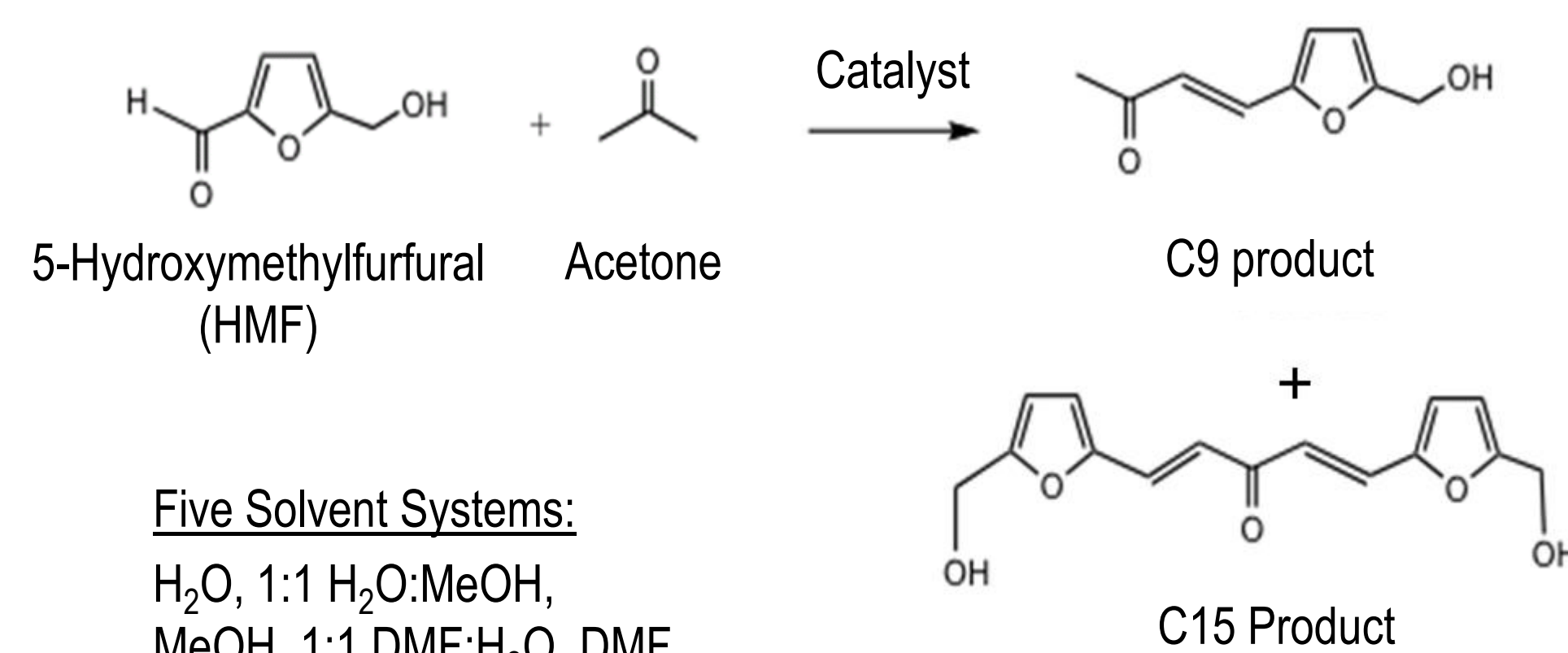


Figure 2. Five different solvent systems were evaluated in order to determine the catalyst's solubility. The catalyst is only soluble in aqueous systems. **Reaction conditions:** 10 mol% catalyst*, 3.0 eqv acetone, 1.0 mL solvent / mmol HMF, RT, 16 hrs.

* The catalyst can not be defined at this time due to intellectual property rights.

Aldol Reaction (continued)

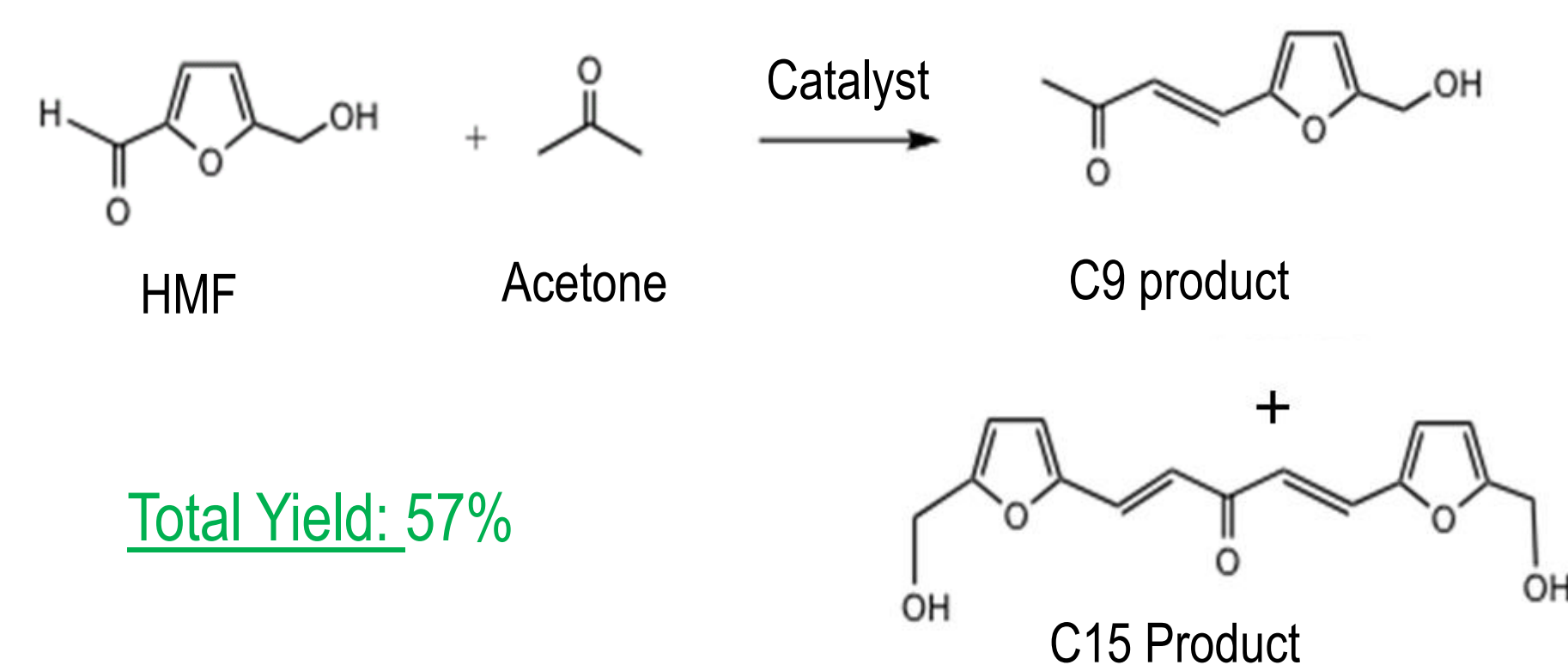


Figure 3. Aldol reaction between HMF and acetone in water. This reaction produces two products, the monomer (C9) and the dimer (C15) product. The yield of this reaction was moderate so the conditions were optimized to get a better yield. **Reaction conditions:** 10 mol% catalyst, 1.0 eqv acetone, 0.5 mL H₂O / mmol HMF, RT, 48 hrs.

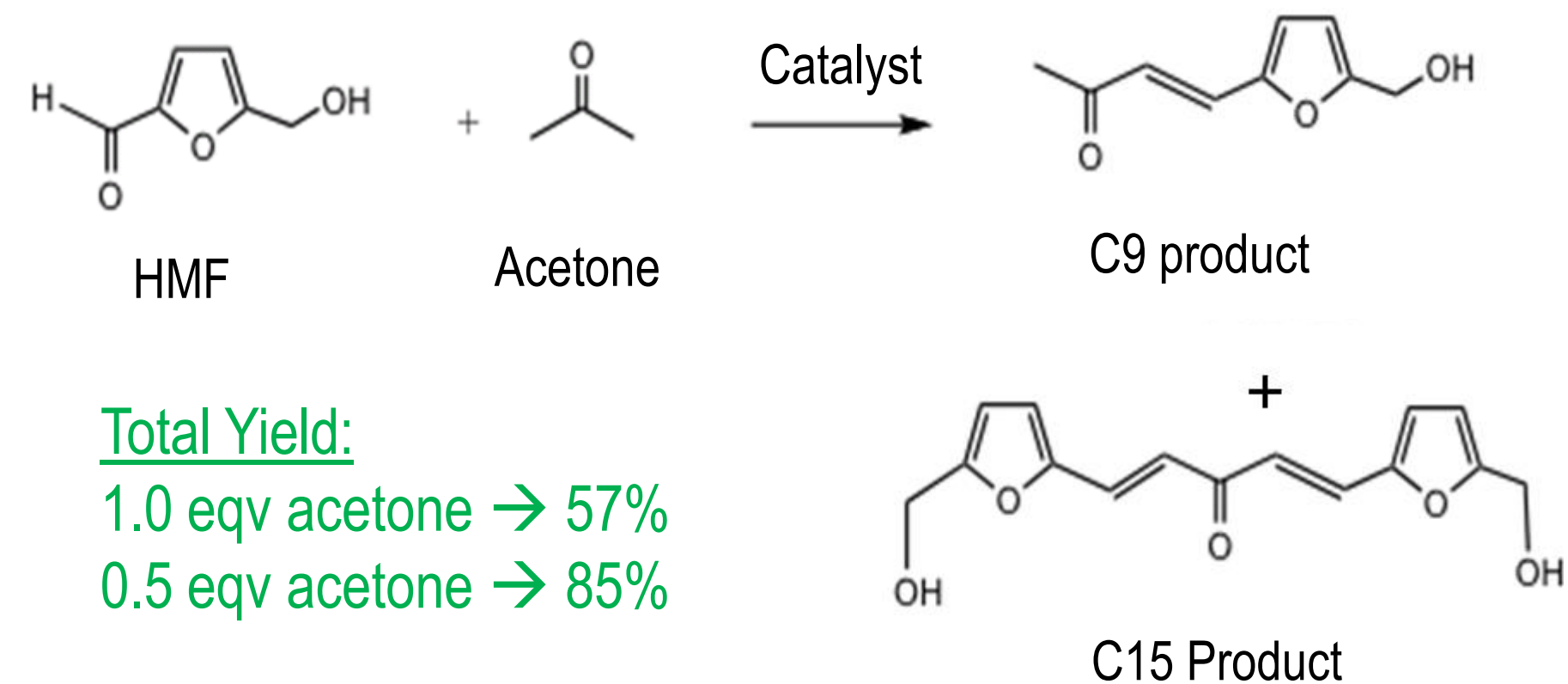


Figure 4. Aldol reaction between HMF and acetone gives a C9 and C15 product. A higher total yield was achieved using 0.5 eqv of acetone. **Reaction conditions:** 10 mol% catalyst, 0.5 mL Bicine buffer / mmol HMF, RT, 48hrs.

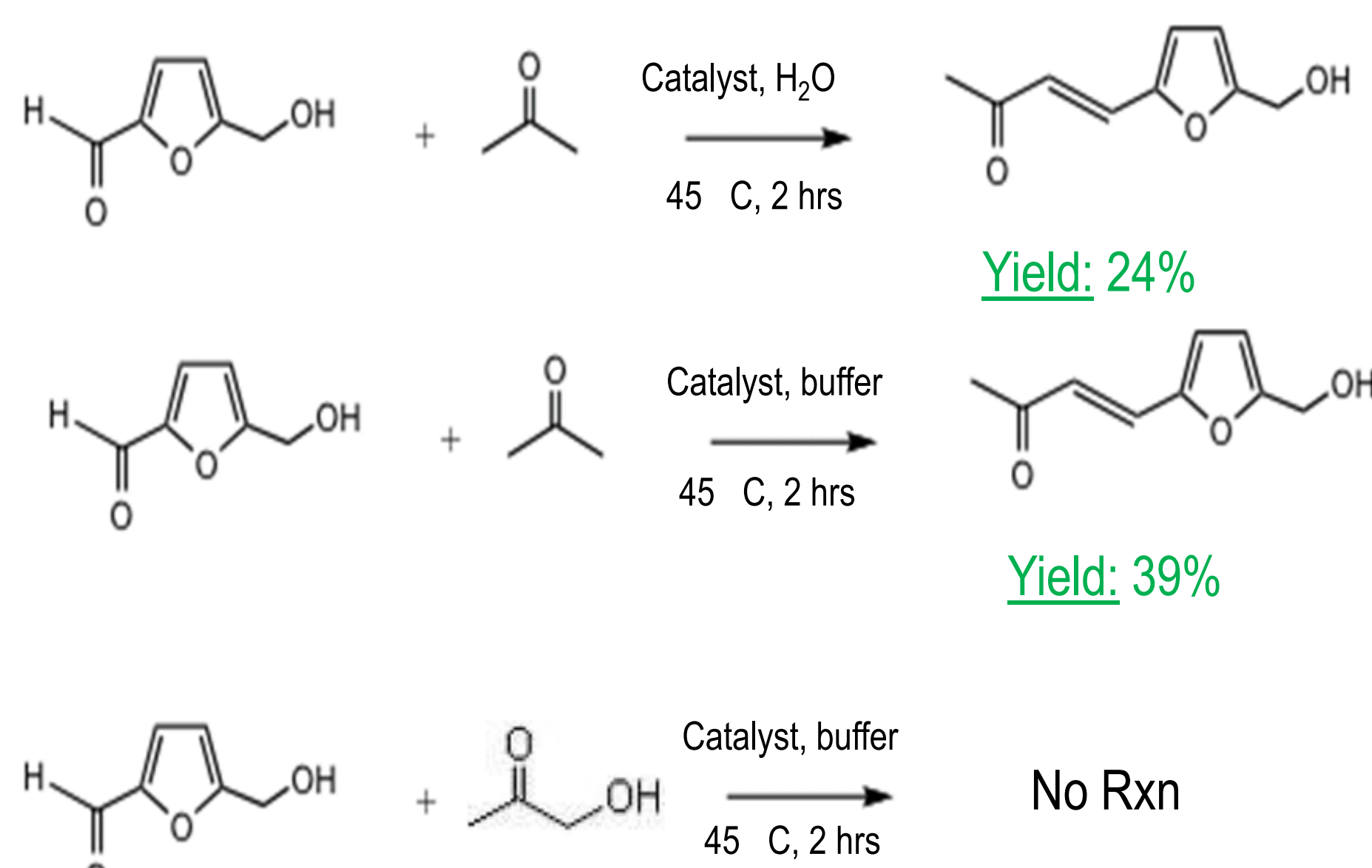


Figure 5. Microwave aldol reactions using HMF and acetone or hydroxyacetone. The reactions with acetone are at higher temperatures, have shorter reaction times, and lower yields versus the previous aldol reactions (Figure 2). Under these conditions, hydroxyacetone doesn't react with HMF.

Indium (III) Chloride Catalyst

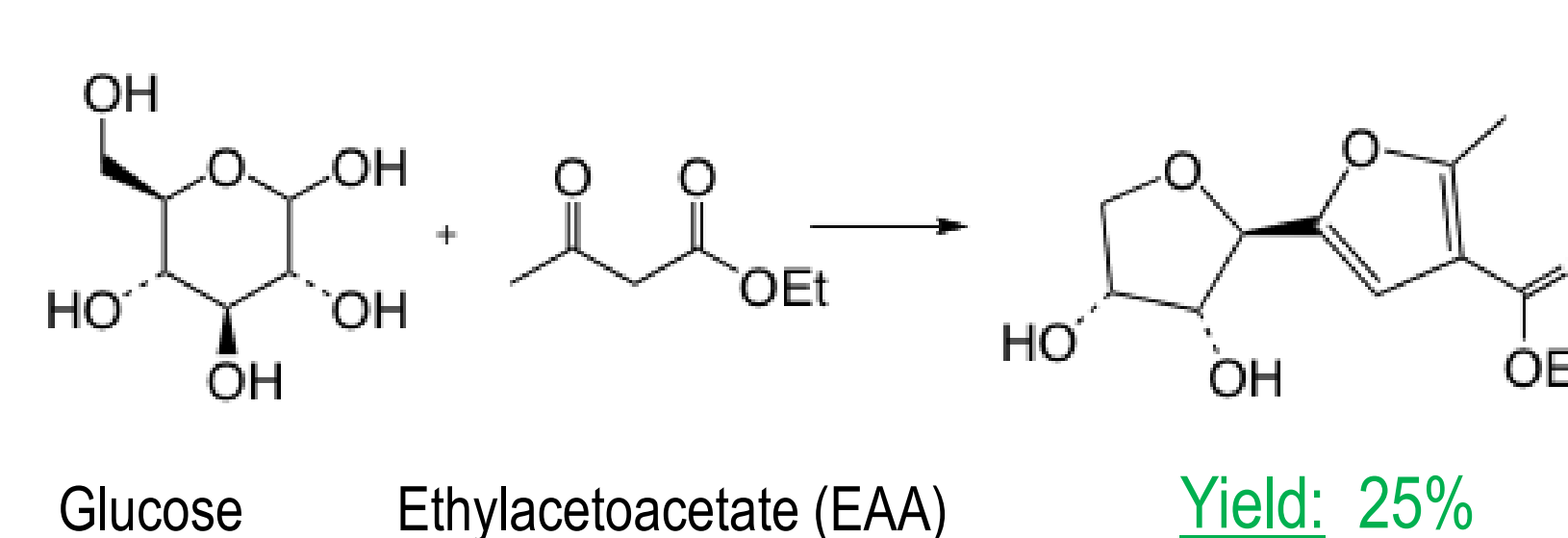


Figure 6. Carbon chain extension reaction using glucose and ethylacetoacetate as the starting materials and InCl₃ as the catalyst. The yield of this reaction was poor so this catalyst was not used for further reactions. **Reaction conditions:** 10 mol% InCl₃, 1.0 eqv EAA, 0.5 mL H₂O / mmol glucose, 80° C, 48 hrs.

Cerium (III) Chloride Catalyst

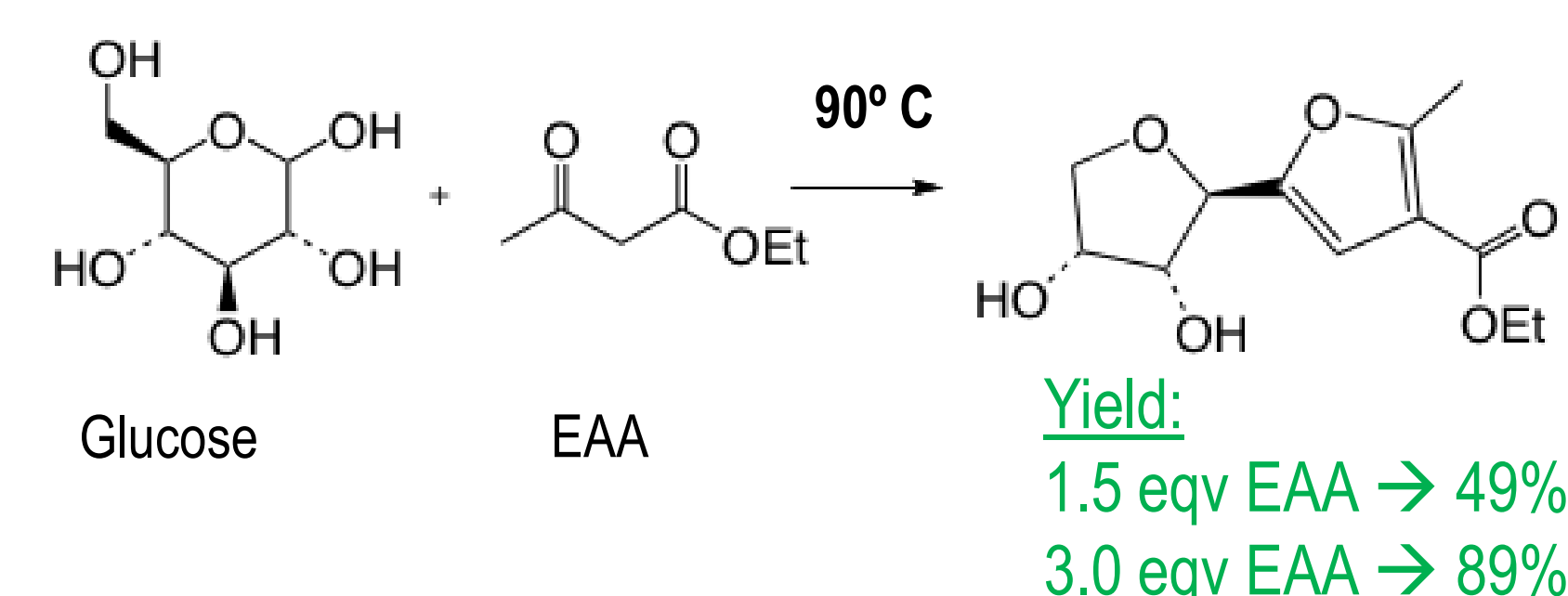


Figure 7. Carbon chain extension reaction using glucose and ethylacetoacetate as the starting materials and CeCl₃ • 7 H₂O as the catalyst. The yield of this reaction using 3.0 eqv EAA was very high so this reaction was repeated several times to determine the ideal conditions. **Reaction conditions:** 25 mol% CeCl₃ • 7 H₂O, 0.5 mL H₂O / mmol glucose, 90° C, 48 hrs.

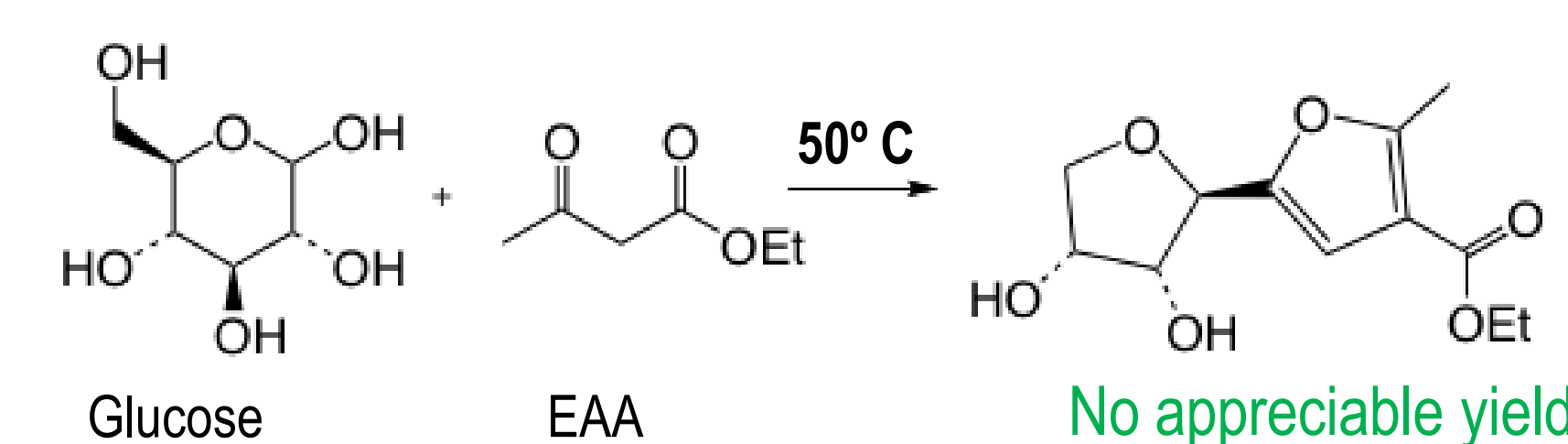


Figure 8. This reaction is the same as the previous CeCl₃ • 7 H₂O reaction except for the reaction temperature which was lowered to 50° C. **Reaction conditions:** 25 mol% CeCl₃ • 7 H₂O, 3.0 eqv EAA, 0.5 mL H₂O / mmol glucose, 50° C, 96 hrs.

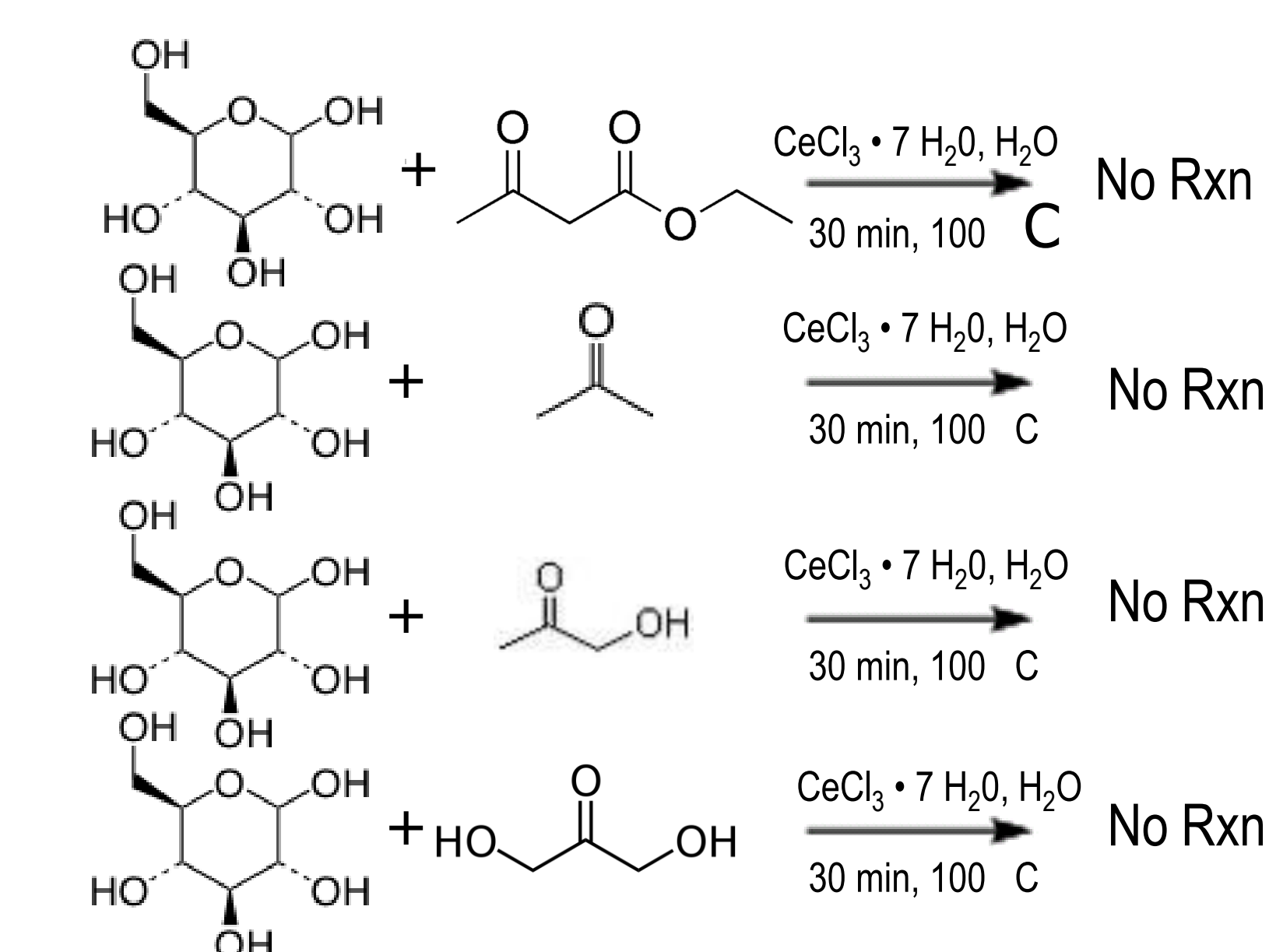


Figure 9. Microwave reactions using glucose and various ketones. Even with the elevated reaction temperatures (as compared to the previous reactions with CeCl₃ • 7 H₂O as the catalyst), the starting materials didn't react. The short reaction time may be the cause.

Lanthanide Triflate Catalysts

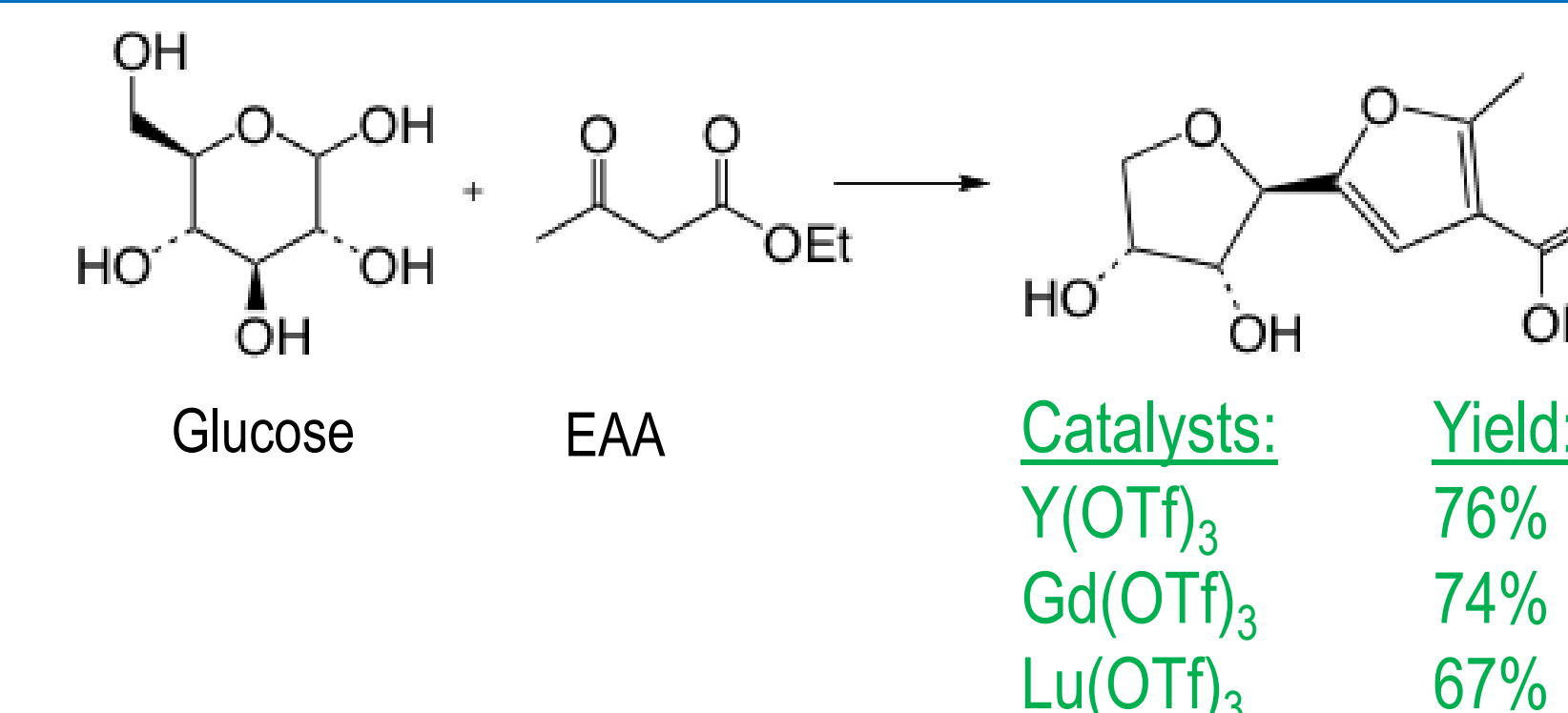


Figure 10. Carbon chain extension using glucose and ethylacetoacetate as the starting materials and three different Lanthanide triflate catalysts. For all three catalysts, the yields were high. **Reaction conditions:** 10 mol% Lanthanide catalyst, 3.0 eqv EAA, 0.5 mL H₂O / mmol glucose, 90° C, 48 hrs.

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112
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Source: <http://www.elementsdatabase.com/>

Figure 11. As general periodic trends, atomic radius decreases from left to right in a period and increases from top to bottom in a column.

Element	Atomic Radius (Å)	Yield of C12 Product
Lutetium (Lu)	2.25	67%
Yttrium (Y)	2.27	76%
Gadolinium (Gd)	2.54	74%
Cerium (Ce)	2.70	89%

Source: <http://environmentalchemistry.com/yogi/periodic/atomicradius.html>

Figure 12. The atomic radii of the Lanthanide catalysts appear to have an effect of the product yield. As the atomic radius increases, the product yield increases as well. However, this trend is general not yet definitive.

Conclusion

- Aldol reaction works best with 0.5 eqv acetone and in buffer
- Indium chloride catalyst give poor yields for reactions with glucose and EAA
- Cerium chloride catalyst gives high yields for reactions with glucose and EAA
- Lanthanide atomic radius has an effect on the product yield
 - No definitive trend has been found
- Overall, these reactions show that biomass-derived glucose can successfully be converted into a longer carbon chain molecule; however, some of the reaction conditions need to be optimized in order for these reactions to become a commercially viable process**

Literature

Indium (III) Chloride reactions: Yadav J, Reddy B, Sreenivas M, Satheesh G. (2007) Indium (III) Chloride/Water: A Versatile Catalytic System for the Synthesis of C-Furyl Glycosides and Trihydroxyalkyl Furan Derivatives. *Synthesis*, 11, 1712-1716.

Cerium (III) Chloride reactions: Misra AK, Agnihotri G. (2004) Preparation of polyhydroxyalkyl- and C-glycosylfuran derivatives from free sugars catalyzed by cerium (III) chloride in aqueous solution: an improvement of the Garcia Gonzalez reaction. *Carbohydrate Research*; 339, 1381-1387.