GREEN CHEMISTRY PERSPECTIVE OF HYDROXY-METHYLFURFURAL MICROWAVE-ASSISTED ORGANIC SYNTHESES

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ABSTRACT

Sintesis senyawa organic dengan microwave (MAOS) ditinjau dari aspek Kimia Hijau (Green Chemistry) menunjukkan hasil yang positif. Sebuah contoh penerapan pada sintesis senyawa organik yang juga hijau yakni hidroksimetilfurfural menunjukkan kebanyakan aspek 12 prinsip Kimia Hijau terpenuhi. Hal ini diperkuat dengan perhitungan atom ekonomi dan efesiensi yang cukup memadai.

Kata kunci: kimia hijau, aspek kimia hijau (HMF), microwave

INTRODUCTION

Green chemistry, also known as sustainable chemistry, is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. There is The Twelve Principles of Green Chemistry: Prevention, Atom Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstocks, Reduce Derivatives, Catalysis, Design for Degradation, Real time analysis for Pollution Prevention, and Inherently Safer Chemistry for Accident Prevention (Xinhua *et al.* 2008).

Microwave-assisted organic synthesis (MAOS)

Microwaves, like all electro-magnetic radiation, travel at the speed of light. They are of relatively low energy and cannot break chemical bonds. They cause heating on a molecular level and can accelerate reactions, leading to a significant time saving and often improving product yields. Microwave heating results from the interaction of the electromagnetic wave with the irradiated medium. The difference between microwave and conventional heating is that in conventional heating heat transfers occur from the heating device to the medium, while in microwave heating heat is dissipated inside the irradiated medium; it is a mass heating, and heat transfers occur from the treated medium to the outside.

MAOS is a new method in organic synthesis by using Microwave energy for heating the reaction. Microwave energy is introduced into the chemical reactor remotely and passes through the walls of the reaction vessel heating the reactants and solvents directly. In contrast, traditional equipment for heating reactions, such as oil baths, sand baths and heating mantles, is not only slow, but also creates a hot surface on the reaction vessel where products, substrates and reagents often decompose. These items in term of Green Chemistry are not preferred.

Microwave dielectric heating drives chemical reactions by virtue of the ability of some liquids and solids to transform electromagnetic radiation into heat. A properly designed vessel allows the temperature increase to be uniform throughout the sample, leading to fewer by products and or product decomposition.

So, even though in term of electric efficiency it is debatable between microwave heating and conventional heating oven, minutes instead of in hours for microwave is completing the reaction only in conventional still having advantages by the time for heater. In the other word, generating microwave for 1 minute would consume much less electric energy than for conventional heater operating for 1 hour. It is the efficient way of electricity consumption.

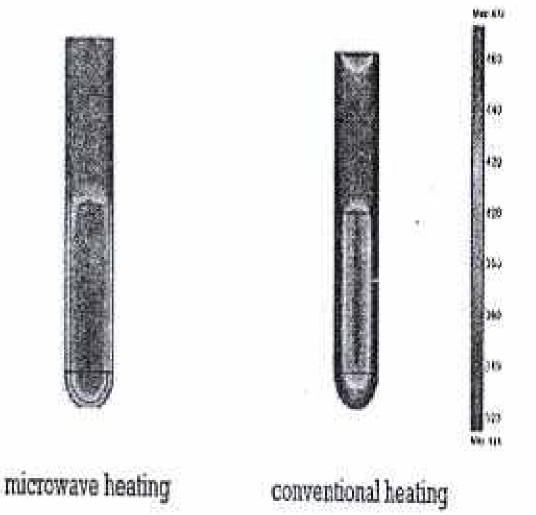


Figure 1 Microwave irradiation results in direct heating of reagents and / or solvents (Roger, 2000).

There are only four permitted frequencies for industrial, medical and scientific use of microwaves: 915 MHz, 2450 MHz (2.45 GHz), 5800 MHz (5.80 GHz) and 27120 MHz (27.12 GHz). The use of low electric consumption microwave is already introduced which only consumes 450-850 watt. This one is much lower from standard microwave which have up to 2.100 watt for heating (Laura, 2005).

Hydroxymethylfurfural (HMF or 5-(Hydroxymethyl)furfural)

5-HMF is an aldehyde and a furan compound formed by decomposition of sugars and carbohydrates. 5-hydroxy-methylfurfural (5-HMF) is a potential intermediate for fine chemicals, pharmaceuticals and furane-based polymers, and has been called a "sleeping giant" as an intermediate(Xinhua *et al.* 2008).

HMF can be converted to 2,5-dimethylfuran, or DMF; DMF can be used as a liquid biofuel that in certain ways is superior to ethanol. Organic oxidation of HMF also gives 2,5-furandicarboxylic acid which may replace terephthalic acid as a monomer in the production of plastics. Recently 5-HMF is considered as a treatment for sickle cell disease.

Conventional methods for synthesizing HMF

The following reaction describes one of the current ways of producing HMF:

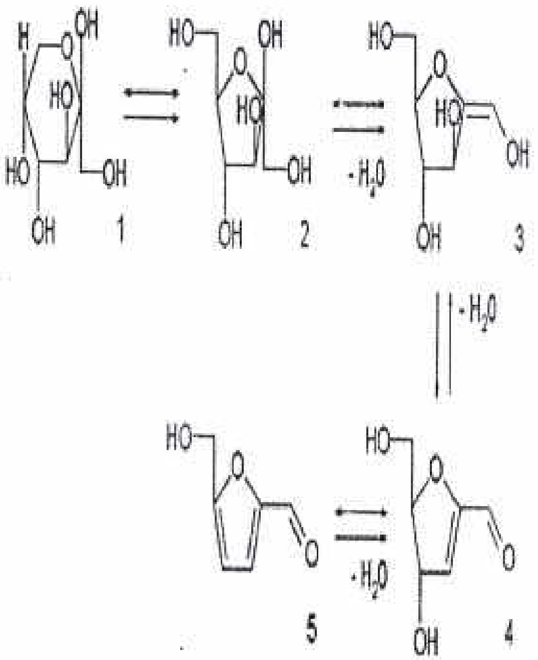


Figure 2: A way of producing HMF; (Label: 1=fructopyranose,2= fructofuranose, 3,4 = two inter-mediate, stages of dehydration, 5= HMF)

In this method, fructose is reacted with HCl in an aqueous phase and the formed HMF (very water-soluble) is then continuously extracted into Methyl isobutyl ketone as an organic phase at 180 °C. The water phase is modified with DMSO and PVP, reducing the amount of side product to a minimum. The organic phase is modified with 2-butanol in order to improve the amount of HMF in the organic phase. In an optimized system for fructose (but not raw biomass), conversion is 77% with half the HMF ending up in the organic phase. Removing the (high boiling) solvent remains an issue (Watanabe *et al.* 2005; Tarabanko *et al.* 2006).

There are some disadvantages of remaining relying on the use the conventional method, and at the other hand the advantage of using MAOS. As a tool for preparative chemistry, micro-wave heating has a number of advantagees; reactions complete in minutes instead of hours, yields can be improved, less by-product formation, new chemistry. In the following chapters, this will be described.

MAOS as a Sustainable Method for synthesizing HMF

This method is proposed by Xinhua Qi, *et al.* 2008; Francisco *et al.* 1998. For considering the Sustainability and Green Chemistry aspect, there are some aspects of greenness we focus on: Green Product (HMF is a green chemical itself), Green Method (MAOS is a green method for synthesizing HMF which we will describe later), Green Feedstock (the reactant used is fructose from biomass which is the sustainable resource promising alternative for the sustainable supply of fuel and valuable chemicals), Catalyst (in deciding the proper catalyst for producing HMF by using MAOS, we consider the proposed H^+ catalysts used so far: mineral acids (such as H_2SO_4, HCl, H_3PO_4), organic acids (such as oxalic acid and levulinic acid), solid acid (such as H-form zeolites and solid metal phosphates), transition metal ions and cation exchange resins.

In term of Green Chemistry, using such catalysts however has drawbacks, such as separation, recycling, corrosion problem, low selectivity and low fructose conversion. Xinhua Qi, *et al.* (2008) and Francisco *et al.* (1998) has proven that ion exchange resin is an alternative which would perform better result and more importantly green catalyst, and a mixed organic-aqueous solvent system is mostly considered as a green alternative, and will be used for MAOS method.

MAOS in term of Energy Efficiency

Among the 12 principles of Green Chemistry, MAOS plays role on Energy Efficiency principle. (MAOS) have much higher yield and selectivity for a given reaction time for many types of reactions. It is the very short time period by direct interaction of microwave energy with the reaction mixture could certainly be considered "green" and highly efficient, because of the reduced energy consumption and the associated time savings.

A study comparing the energy efficiency between a conventional oil bath organic synthesis and a MAOS has indicated that a significant energy savings (up to 85-fold) can be expected for most chemical transformations using microwaves as an energy source on a laboratory scale.

RESEARCH METHOD

Xinhua Qi's Ways for ending up with optimum result

After series of experiments with many variables, Xinhua found that solvent composition is acetone–water mixture of 70 : 30 (w/w). A reaction temperature of 150 °C was chosen as the best temperature since fructose converseons and 5-HMF yields were high and levulinic acid yields were low.

High 5-HMF yields with high fructose conversions were obtained under milder conditions, recyclable catalyst and moderate temperatures with the present method. Since in green engineering, the recycling of catalyst is very important in practice, it has been concluded that the resin was stable in this system and the nearly constant fructose conversions and 5-HMF yields verified this conclusion.

Microwave irradiation was remarkably more efficient not only for fructose conversion, but also in achieving high 5-HMF yields. When the reaction mixture was heated by sand bath, the fructose conversion and 5-HMF yield was 22.1% and 13.7%, respectively, at a reaction time of 10 min, while the corresponding value for microwave heating was 91.7% and 70.3%, respectively.

Table 1. Term of Green Chemistry Principles

No	Principle	Applicability	Remarks
1	Prevent Waste	Applicable	This process almost creates no waste or side products not used.
2	Design safer chemicals and product	Applicable	Both reactant and product is considered green chemicals
3	Less Hazardous Chemical Syntheses	Applicable	Both reactant and product is considered green chemicals
4	Use renewable feedstock	Applicable	The reactant fructose is from biomass.
5	Use catalyst	Applicable	strong acid cation exchange resin as a green catalyst
6	Avoid chemical derivatives	Applicable	there is no derivative, except rehydration product oh HMF, levulinic acid and formic acid
7	Maximize atom economy	Applicable	70% atom economy is quiet good.
8	Safer solvent and reaction conditions	Applicable	a mixed organic-aqueous solvent
9	Increase energy efficiency	Applicable	MAOS only uses electricity
10	Design chemicals and product to degrade	Applicable	Both reactant and product is considered green chemicals from biomass which organic compound which can degrade easily.
11	Analyze in real time to prevent pollution	Applicable	
12	Minimize the potential for accidents	Not yet considered	

THE PROCESS IN TERM OF 12 PRINCIPLES OF GREEN CHEMISTRY

MAOS method is quite appropriate in term of Green Chemistry Principles. The table below gives the overview of it.

Calculation of Atom Economy, Atom efficiency and The E-factors

Atom Economy, Atom efficiency and The E factors are the useful measures of the potential environmental acceptability of chemical processes. Atom Economy is a calculation of how much of the reactants remain in the final product. Atom efficiency is calculated by dividing the molecular weight of the desired product by the sum of the molecular weights of all substances produced in the stoichiometric equation, or in another definition: Atom Efficiency = %Yield x Atom Economy

Atom Economy is a calculation of how much of the reactants remain in the final product.

% Atom Economy

= (FW of atoms utilized/FW of all reactants) x 100%

$$= \frac{126}{180} x100\% = 70\%$$

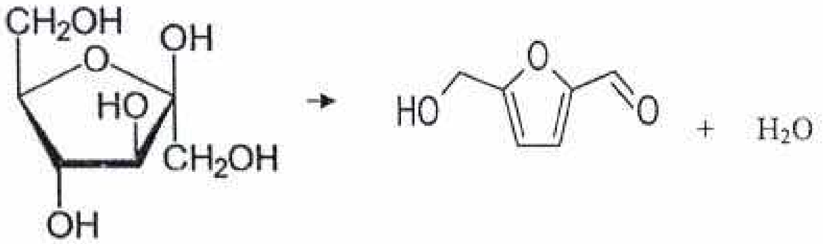
So the atom economy is 70%.

Atom Efficiency = %Yield x Atom Economy

= 73.4x 70%

= 51.38%

The use of acetone–water reaction media resulted in yields of 5-HMF as high as 73.4% for 94% conversion at 150 °C



Fructose	→	5-HMF	+	H_2O	
$C_6H_{12}O_6$	→	$C_6H_6O_3$	+	$3H_2O$	
Mr= 180.16 g mol^{-1}		126.11 g/mol			18 g/mol

Table 2. Atom Economy

Reagent Formula	Reagent FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Utilized Atoms
$C_6H_{12}O_6$	180	6C, 6H, 3O	(6x12)+(6x1)+(3x16) = 126	6H, 3O	18
Total 6C,12H,6O	180	6C, 6H, 3O	126	6H, 3O	18

Table 3. Use of acetone–water reaction media

Reactant	Fructose	$C_6H_{12}O_6$	Amount	mol	Mr
			5 g	0.028	180
Solvent	H_2O-aceton	H_2O-C_3H_6O	70:30 (w/w)		
Product	5-HMF	$C_6H_6O_3$	Yield 73.4%		126

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