



Hydrothermal gasification of *Rosa Damascena* residues: Gaseous and aqueous yields



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ABSTRACT

The gasification of *Rosa Damascena* residues – by-products of the rose-oil industry – was investigated under hydrothermal conditions at 500 °C and 600 °C, 35–45 MPa pressure with a reaction time of 1 h. The experiments were performed in the absence and presence of catalysts of K₂CO₃ and trona in a batch type reactor. The composition of the gaseous and aqueous products was determined by gas chromatography and high performance liquid chromatography, respectively. H₂, CO₂ and CH₄ are the main gaseous products while carboxylic acids (formic acid, acetic acid, glycolic acid) are the main components found in the aqueous phase followed by furfurals, phenols, aldehyde and ketones. More gaseous products were obtained at the higher temperature of 600 °C. Adding catalyst was found to aid the conversion process but the effect was only slight. *Rosa Damascena* residues have the potential to be a useful source for H₂ production in the future.

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1. Introduction

The need for energy is continuously escalating due to increasing world population and the energy demands of technological innovations. Fossil oil is the major energy resource which fulfills the fuel requirements of the modern world. However, it is a limited resource that is steadily reducing. At the same time, climate change and environmental issues require action to curb greenhouse gas emissions. There is a pressing need for alternative, clean energy sources [1–3]. Biomass is one such alternative energy source which may have the potential to contribute to future energy supplies [4].

The term biomass covers a broad range of materials that are all derived from living organisms, such as agricultural residues, poultry waste or sewage sludge. Also, biomass as a renewable and sustainable energy source can develop over relatively short periods, ranging from a few hours to a few years. Furthermore, biomass does not take millions of years in development as does the formation of petrol. It is a clean energy source compared to fossil fuel, with CO₂ emission levels of close to zero readily achievable.

For several thousand years biomass has been best known as an energy source in the form of wood, and used extensively for domestic cooking. In the modern age, the energy density of biomass can be raised and converted into fuels suitable for use in the transportation and electricity generation sectors [5].

The energy density of biomass can be raised by various conversion technologies. For example, biogas [6], bioethanol [7], biodiesel [8] production from biomass, bio-oil by pyrolysis [9–11] are technological processes where the end product has a much higher energy density than existed in the original biomass form. And of particular note, wet biomass gasification under hydrothermal conditions is a developing technology for H₂ production [12].

The term 'hydrothermal' is used to describe water at higher temperatures and pressures. Specifically, sub- and supercritical water, refer to the state of water below and above its critical temperature and pressure ($T_c = 374\text{ °C}$, $P_c = 22\text{ MPa}$). Thermo physical properties of water are very different under hydrothermal conditions, especially in supercritical conditions where water becomes a good solvent for organic molecules, and a very suitable medium for organic reactions [13,14]. By decreasing the dielectric constant of water, organic species and gases become miscible with water above its critical point, which reduces the mass transfer limitations of the reactions [15]. Another important property of water is its ion product (K_w). At ambient conditions, water has a K_w of $10^{-14}\text{ mol}^2/\text{kg}^2$. As the temperature increases at constant pressures, the value of K_w increases up to 300 °C and then starts to decrease again. K_w

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is $\sim 10^{-11}$ mol²/kg² at 23 MPa and 250 °C while $\sim 10^{-23}$ mol²/kg² at 25 MPa 600 °C [16]. Water behaves not just as a medium, but rather as an active participant in the chemical reactions [17,18]. Hence, water under hydrothermal conditions supports the biomass degradation and enhances H₂ production.

Lu et al. [19] gasified the corn cob biomass feedstock at 823–923 K, and a pressure of 22.5–27.5 MPa. H₂ was the main gaseous product obtained. Temperature is the most important parameter to achieve max. H₂ yield and high biomass gasification conversion. Pre-treatment of biomass by acids can also improve the H₂ yield.

Rice straw was converted into the valuable product of H₂ with hydrothermal treatment [20]. The efficient conversion was achieved by two-stage processing: the hydrolysis of constituents – hemicellulose, cellulose, lignin – to glucose and xylose as stage one, with the second stage being the production of H₂ from the organic residue.

Serani et al. [21] demonstrated the supercritical water gasification of aqueous distillery waste from beet, sugarcane, cereal and wine-producing. The experiments were performed in a 100 ml batch reactor, at 400–500 °C and at a max. pressure of 35 MPa with 1 h residence time. At the end of gasification, solid (3.5 wt.%), liquid (89 wt.%) and gaseous (4 wt.%) products were obtained. The gaseous phase has CO, CO₂, H₂ and CH₄. The amount of the gas produced increased to 5 wt.% and H₂ to max. 65 mol% when the temperature increased from 400 to 500 °C. It is concluded that the gasification and production of H₂ are more efficient at higher temperatures.

H₂ yields can be increased in biomass gasification by the use of catalysts. Lignocellulosic sunflower stalk and corn cob are gasified in a batch autoclave at 773 K and 32 MPa average pressure by using cheap and disposable catalysts such as K₂CO₃, trona and red mud [22]. H₂ yields were increased dramatically (more than 100%) by the use of catalysts.

Since biomass consists of many different compounds which are all reacting in different ways under hydrothermal conditions, the chemistry of biomass degradation is rather complex. Therefore, using model compounds can help in understanding the gasification mechanism [23]. Susanti et al. [24] reported the glucose gasification as a model substance for cellulose in supercritical water at 873–1040 K and 25 MPa. H₂ gas yields as main product could reach to 11.5 mol/mol glucose at 1040 K and 1.8 wt.% lower glucose concentrations with 91% glucose conversion ratio to gaseous products of H₂, CO₂, CO and CH₄. It is concluded that the gasification mechanism is still very complex, including hydrolysis, steam reforming, water–gas shift reaction, methanation and other reactions. Details on hydrothermal gasification in relation to various kinds of real biomass or biomass model compounds can be widely found in the literature [25–29].

H₂ from biomass could be one solution to demand for the production of clean energy. All kinds of organic waste from industry can be regarded as biomass resources and assessed for their energy potential, rather than simply being abandoned to decay. In this study, wet *Rosa Damascena* residues were gasified under hydrothermal conditions to investigate the H₂ yield. The oil obtained from the *Rosa Damascena* oil rose is one of the most widely-used essential oils in the cosmetic industry and this type of oil rose is mostly grown in Turkey, which produces 70% of the world's total rose oil supply [30–32]. Rose oil is extracted from the flowers by steam distillation or solvent extraction. After the oil production processes are complete, approx. 1500 tons of residues are released every season (two months running from May to June) and left to decay naturally. This study shows for the first time that *Rosa Damascena* residues with high water content can be gasified into a high value product of H₂ gas under hydrothermal conditions. The conversion was investigated in the absence and presence of K₂CO₃ and trona as catalysts.

Table 1
Properties of samples.

Property	Raw rose (GS)	Water extract waste (GSD)	Hexane extract waste (GH)
Moisture (%)	5.71	6.00	4.63
Ash (%)	4.40	5.50	6.99
Cellulose (%)	27.56	31.87	32.61
Hemicellulose (%)	13.10	24.80	22.35
Lignin (%)	10.33	15.53	15.41
Extractives (%)	36.34	29.81	23.75
C (%)	46.83	47.00	47.58
H (%)	3.61	6.34	6.58
N (%)	2.72	2.68	3.10
S (%)	0.09	0.11	0.12
TOC (%)	47.33	47.92	46.49

2. Materials and methods

2.1. Material

Rosa Damascena residues from treatments of water distillation (GSD) and n-hexane extraction (GH) and raw rose plant (GS) were collected from ERÇETİN Rose-oil Company in Isparta/Turkey in June, 2012. The samples were dried in the open air, ground and sieved through a 0.1 mm sieve. All samples were analyzed for CHNS/O amounts by Elemental Analyser (Thermo Scientific Flash 2000). Moisture and ash content of raw materials were determined according to ASTM methods. Cellulose, hemicellulose and lignin amounts of the samples were analyzed by the P.J. Van Soest method [33]. The characterizations of dry samples are given in Table 1.

Sample names are nomenclatured as: *Sample name mark, Catalyst mark, and Temperature mark*. The catalysts K₂CO₃ and trona are marked as “K” and “T”, respectively. Experimental temperatures of 500 °C and 600 °C are abbreviated as “T5” and “T6”. GST5 shows the raw rose sample (GS) gasification at 500 °C (T5), GSTT6; raw rose sample (GS) gasification at 600 °C (T6) in the presence of trona (T).

K₂CO₃ (Sigma–Aldrich, ≥99.0% purity) and trona (89.2 wt.% main constituent of Na₂CO₃NaHCO₃·2H₂O, 0.6 wt.% insoluble fraction, mined in Beypazarı-Turkey) were used as catalysts without further purification, in concentrations of 10 wt.% on biomass base.

2.2. Experimental procedure

1.2 g of biomass sample and 15 ml of deionized water with or without catalyst were placed into a SS-316 stainless steel batch type reactor. The volume of the reactor is 100 ml. Gasification experiments were performed at 500 and 600 °C. The air inside the reactor was swept by inert N₂ gas stream for 5 min. The reactor was closed tightly and placed into a pre-heated oven. The heating rate of the reactor was 8–10 °C/min until the desired temperature was reached after approx. 45 min. The reactor assembly included a rotating shaker with an eccentric and a temperature controller with a PID controller shown in Fig. 1. The experimental set-up is explained in detail elsewhere [34].

The reaction time was set at 1 h at the desired experimental temperature, and the max. pressures reached for all reaction temperatures in the absence and presence of catalysts are given in Table 2. After each run, the reactor was taken from the oven and cooled down to room temperature with electrical fans, the cooling process taking approximately 3 h. The reaction time does not include preheating and cooling times.

The volume of gaseous products was measured with a gasometer in ±10% error, and gas samples were taken by using gas tight syringes and analyzed by gas chromatography (Agilent Technologies HP 7890A, USA) equipped with serially connected Hayesep Q 80/100 mesh (0.5 m long × 2 mm i.d.), Hayesep Q 80/100 mesh (1.8 m long × 2 mm i.d.), Molsieve 5A 60/80 mesh (2.4 m

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