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Wine Grape Residues Gasification in Supercritical Water

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***Abstract*—**In this study, production possibilities of hydrogen and/or methane via SCWG from black grape residues have been investigated. For this aim, grape residues which remain as a by-product of the wine making process have been used. Since utilization from grape residues is limited due to the high moisture content, supercritical water gasification is the most convenient method. The effect of the gasification temperature and type of catalyst on supercritical water gasification have been investigated. Gasification experiments were performed in a batch autoclave at four different temperatures 300, 400, 500 and 600°C. K_2CO_3 and Trona ($NaHCO_3.Na_2CO_3{\cdot}2H_2O$) were used as catalyst. Real biomass types of black grape residues have been successfully gasified and the product gas (hydrogen, methane, carbon dioxide, carbon monoxide and a small amount of ethane and ethylene) were identified by using gas chromatography. A TOC analyzer was used to determine total organic carbon (TOC) content of aqueous phase. The amounts of carboxylic acids, aldehydes, ketones, furfurals and phenols present in the aqueous solutions were analyzed by high performance liquid chromatography. When the temperature increased from 300°C to 600°C, mol% of H_2 in gas products increased. The presence of catalysts improves the hydrogen yield. Trona showed gasification activity to be similar to that of K_2CO_3. It may be concluded that the use of Trona instead of commercially produced catalysts, can be preferably used in the gasification of biomass in supercritical water.

***Keywords*—**Biomass, hydrogen, grape residues.

I. Introduction

THE objective of the investigation presented here is to support the utilization of waste and residual biomass for energy production and to produce a valuable gas for hydrogen production using supercritical gasification. The conversion of wet biomass under hydrothermal conditions is a suitable alternative to the classical gasification technologies, which require energy for drying the biomass.

There are numerous methods for waste-to-energy conversion, including thermo chemical conversion such as gasification, pyrolysis, liquefaction and combustion. Supercritical water gasification (SCWG) is one of the most promising technologies for converting high moisture biomass to a pressurized and clean gas with high hydrogen content [1-11]. The most important potential sources for wet biomass materials are unevaluated parts of all plants, vegetables and fruits residues which are being products of photosynthesis and they can be used for sustainable production of hydrogen.

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Wet waste biomass streams available for the production of energy fuels are not suitable for classical gasification processes, because of their high water content (>70 %) [1]. By increasing of moisture content of biomass, energy production of different gasification technologies like gasification, pyrolysis and liquefaction decreases.

Supercritical gasification offer attractive alternatives for the conversion of wet biomass to useful products. It is appropriate for production of both H_2 and CH_4 and these valuable gases can be generated at an elevated pressure. Pre-drying of biomass materials are not necessary, which is an energy and time consuming step. The other important advantages of SCWG are considered as follows: it is operated at lower temperatures, smaller reactor volumes are required because of high reaction rate, CO formation is very low, thus reforming process is not required, and formation of tar and coke is much lower.

Supercritical water gasification process has attracted worldwide attention because of the characteristics of water as a reaction medium. Forschungszentrum Karlsruhe in Germany, National Institute for Resources and Environment in Japan, Hawaii Natural Energy Institute, U.S. Pacific Northwest Laboratory and other research centers have had many detailed studies on SCWG of some organic compounds to produce hydrogen [12-19]. Gasification of model compounds (cellulose, glucose, xylan and lignin) in supercritical water can be considered as a good model for the gasification of the more complex residues and wastes in supercritical water [20-23]. Serani et al. investigated supercritical water gasification of wine distillery wastewaters at various temperatures in a batch reactor [4]. In another work wastewaters from vinasses and alcohol distillery wastewater have been tested in a continuous flow system by SCWG. The influences of temperature, amount of catalysts addition on the gas phase were studied by Jarana et. al [11].

In this study, sub-and supercritical water gasification of black grape residues were performed in a batch reactor system at a temperature range of 300-600°C. For this aim, grape residues which remain as a by-product of the wine making process have been used. The wine production resulting in a rest product with a moisture content of about 70-80%. Since utilization from grape residues is limited due to the high moisture content, supercritical water gasification is the most convenient method. The effects of the gasification temperature and type of catalyst on supercritical water gasification have been investigated. K_2CO_3 and natural mineral catalyst Trona ($NaHCO_3.Na_2CO_3{\cdot}2H_2O$) were used as catalyst.

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The effectiveness of naturally occurring mineral catalyst is important to the development of a commercial biomass gasification process. Use of these materials instead of commercially produced catalysts, would be more favorable to process economically.

II. Experimental

A. Materials

For the tests grape residues, which remain as a by-product of the wine making process (Yazgan Wine Factory, TURKEY) have been used. Grape residues were dried at open-air conditions. This biomass sample was grounded in a crush mill and sieved to obtain a particle size less than 500μm fraction. Elemental analysis of black grape residues were performed) in Laboratories of Izmir Institue of Technology using an elemental analyzer (CHNS-932 by Leco, MI-USA). Proximate and ultimate analysis of the biomass sample was given in Table I. Cellulose, hemicellulose and lignin content of biomasses were analyzed by method of P. J. Van Soest [24] and given in Table II.

The supercritical water gasification of grape residues were performed without and with adding 10 wt.% of potassium carbonate (K_2CO_3) and Trona ($NaHCO_3.Na_2CO_3 \cdot 2H_2O$) as catalyst. K_2CO_3 and Trona were dissolved in water to obtain concentration of 10%wt. Trona is mined as the primary source of sodium carbonate, it has replaced the Solvay process used in most of the world for sodium carbonate production. Purity of Trona as natural mineral catalyst was 89 wt. %, remaining part is moisture (10.4 wt. %) and insoluble fraction is SiO_2 (0.6 wt.%).

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS OF GRAPE RESIDUE

	Grape Residue
Proximate analysis (dry, wt.%)	
Moisture	10.0
Ash	5.98
Crude Protein	12.15
Ultimate analysis (dry, wt.%)	
C	51.30
H	6.44
N	1.96
S	0.14
O (from difference)	35.74
K	2.46
Ca	1.26
Mg	0.19
Al	0.11
Fe	0.10
Cr	0.01
Cu	0.26
Mn	0.01
Zn	0.02

TABLE II
THE COMPOSITION OF GRAPE RESIDUE

Components (daf, wt.%)	Grape Residues
Cellulose	15.19
Lignin	42.83
Hemicellulose	9.44
Extractives	30.45

B. Experimental Procedure

The reactor was a batch-type device made of stainless steel with an internal volume of 100 mL and designed to with stand a pressure of 40 MPa and a temperature of 650°C. Inside the reactor there is a pipe in which thermocouple is fastened for temperature measurement. The temperature and pressure are controlled by the analogue manometer and thermocouple. Mixing was achieved by a motor-driven tumbling movement. In the tumbling reactor, hydrogen yield decreases when heating rate decreases. This heating rates and the final temperature are adjusted by a temperature controller with a PID controller. Schematic presentation of batch autoclave was given in a previous study [25].

To examine the effect of temperature on the gas yield and composition, desired amount of grape residues (1.2g of biomass/15 ml of water) and 10 wt.% of catalysts (0.12 g) were well mixed and loaded into the reactor. And to see the catalyst effect, the experiments were performed without and with adding catalysts.

After loading, the autoclave is flushed by nitrogen for 5 min. to remove all air in the reactor. The reactor was heated to the desired temperature at 6 K min^{-1} and held at the reaction temperature using a PID temperature controller for 60 min. At the end of each run, the reactor was rapidly cooled by quenching in cold water and allowed to reach the room temperature. Volume of the gaseous product was measured by a gasometer after expansion to ambient pressure and gas samples were taken using gas tight syringes for analysis by gas chromatography. The gas volume was measured in ±10% accuracy. Liquid and solid products that remained in the reactor after gas sampling were washed out with water and filtrated to separate solid residue (coke). pH of aqueous products was lowered to 2 by addition of 1-2 drops of concentrated sulphuric acid, which was required to inhibit ionization of organic acids. After each experiment, reactor was washed with tetrahydrofuran (THF) and water to reduce plugging problems caused by solid material. THF was evaporated under vacuum by using a rotary evaporator and the amount of this product (tar) was found extremely low compared with the filtrated solid (char). Total of char and tar were called as residue.

C. Analytical Methods

Gas and liquid products were analyzed by gas chromatography (GC) and high performance liquid chromatography (HPLC). A gas chromatograph (HP 7890A, Wilmington–USA) was 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 long × 2 mm i.d.), Hayesep Q 80/100 mesh (0.9 m long × 2 mm i.d.), Molsieve 5A 60/80 mesh (2.4 m long × 2 mm i.d.), DB-1 (pre-column) and HP-Plot Al2O3 S (25 m long × 0.32 mm i.d.) columns. Two thermal conductivity detectors (TCD) and a flame ionization detector (FID) were arranged serially. Helium was used as carrier gas and oven temperature program was in the following: the GC oven temperature was held at 60°C for 1 min., then ramped to 80°C

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at a rate of 20°C/min, and ramped to 120°C at a rate of 30°C/min, and finally held at 120°C for 2.66 min. A standard gas injection volume of 20 ml was injected twice for all gas samples. The concentration of the gas species was taken as an average of the two injections. The standard deviation is typically less than 2% of the reported value. GC was calibrated with standard gas mixture supplied by HatGaz Company in Kocaeli, Turkey. Gas products were identified by retention time and quantized by external calibration against the standard gas mixture.

The obtained liquid phase was analyzed by HPLC system for the identification and quantification of the products. All HPLC analyses were carried out using a Shimadzu LC-20A series liquid chromatography device equipped with an Inertsil ODS-3 (250 mm length x 4.6 i.d.) column. The HPLC system consists of a DGU-20AS degassing module, LC-20AT gradient pump, CTO-10ASVP chromatography oven and SPD-20 multi-wavelength ultraviolet detector. Analysis of calibration standards was repeated for 5 times and calibration curves were prepared by plotting a linear regression of the average response factor versus analyze concentration. The amounts of carboxylic acids, aldehydes, ketones, furfurals and phenols were measured by the HPLC. Carboxylic acids, phenols and furfurals were analyzed according to Method I (mobile phases: A: 0.05 vol.% H_3PO_4 (pH: 2.25) B: CH_3CN/H_2O (80/20: vol./vol.), flow rate: 1 mL/min, detector: UV, low temperature gradient program of mobile phase and detector: 0 min 90% A and 10% B, 0 min detector wave-length 210 nm, 5 min detector wavelength 290 nm, 7 min detector wavelength 285 nm, 11 min detector wavelength 278 nm, 15 min detector wavelength 232 nm, 17 min 90% A and 10% B, 19 min detector wavelength 290 nm, 25 min 65% A and 35% B, 27.5 min detector wavelength 290 nm, 55 min 65% A and 35%, column temperature: 30 °C). The aldehydes and ketones were analyzed by applying Method II (mobile phases: A: water – B: methanol, flowrate: 1 mL/min, detector: UV (at 365 nm), low temperature gradient pro-gram of mobile phase: 0 min 35% A and 65% B, 5 min 35% A and 65% B, 15 min 15% A and 85% B, 30 min 10% A and 90% B, column temperature: 30 ◦C). The aldehydes and ketones were derivatized to their hydrozone forms by addition of 2,4-dinitrophenylhydrazine into aqueous samples. 2,4-dinitrophenylhydrazone forms of aldehydes and ketones were separated by reversed-phase high-performance liquid chromatography as the same method described in the literature [26].

For the interpretation of the carbon recovery of the experiment it was necessary to measure the carbon amount in all phases (gas, aqueous and solid phase). The aqueous phase was analyzed by a total organic carbon (TOC) analyzer (Shimadzu, model TOC-V_{CPH}). Standard solutions for the calibration were prepared by using potassium hydrogen phthalate. Solid sample module of the TOC analyzer (Shimadzu TOC-V_{CPH}-SSM-5000A) was used to determine the total organic carbon (TOC) content of the solid residue. In order to provide precise data, the samples were analyzed in three times, and the averages were reported as results. The concentration of total phenols was determined by using Jenway Colorimeter (Model 6051, UK). Light source is tungsten filament lamp and measurements were performed at 470 nm.

III. Results and Discussion

To examine the effect of temperature and catalyst type during hydrothermal gasification of grape residues, four runs were conducted over a temperature range from 300 to 600°C. In this paper, we present a study of the catalytic effect of potassium carbonate (K_2CO_3), and Trona catalysts for SCWG of grape residues. In the experimental tests, a reaction time of 60 min has been applied, because the reaction time turned out to be sufficient to reach the maximum conversion at the lowest typical SCWG temperature under noncatalytic condition. Black Grape residues were carried out for the first time to investigate SCWG using a batch reactor. Experiments were performed in the absence and presence of 10 wt% catalysts. Since the experiments were repeated at least three times, the average yield could be evaluated and the reproducibility could be confirmed.

Experimental results are presented in terms of gas yields (mol gas/kg grape residues) and carbon gasification efficiency (CGE, %). In this study, CGE is defined as the ratio of the total moles of carbon in the gas products to the moles of carbon in the biomass feed. For the calculation of the carbon recovery of the experiments, carbon amount measured in all phases (gas, aqueous and solid phase) and carbon balance of products closed within 95–99%. Carbon liquefaction efficiency (CLE) and Residue efficiency (RE) are calculated as the ratio of the total moles of carbon in the aqueous phase and in the solid phase, respectively, to the moles of carbon in the feed. The missing carbon in the balance may be due to by-products such as sticky polymers formed and smeared on the inside walls of autoclave, cannot be analyzed.

A. Effects of Temperature and Catalyst on Conversion of Biomass

Fig. 1 shows the results of product efficiencies (CGE, CLE and RE). As expected the gasification was improved with temperature and by using catalyst. Fig. 1 depicts that K_2CO_3 and Trona have similar catalytic activity for the CGE over the temperature range examined and their gasification efficiency increased to the values of 69.1 and 68.2% at 600°C, respectively. The onset temperature of the degradation reactions was lowered by alkali catalysts, which reduces the formation of residue (char/tar). In the presence of catalysts, CLE was found to be higher resulting with fewer residues (RE). The lowest RE at 600 °C and 20.0 MPa were found in the presence of Trona.

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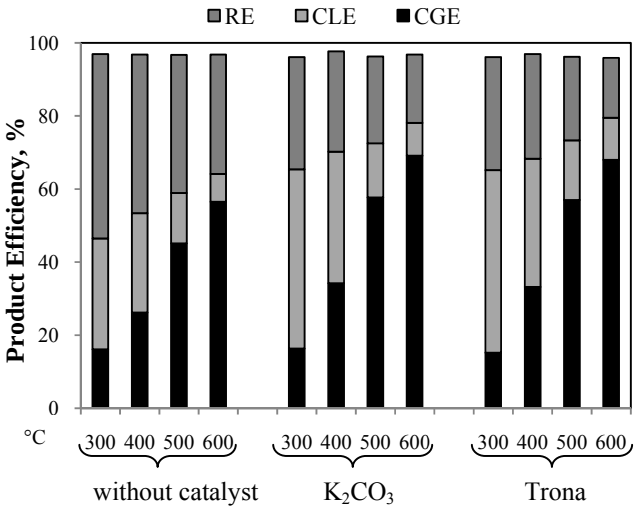


Fig. 1 Variation of product efficiency with temperature and catalyst for SCWG of Grape residues

B. Effects of Temperature and Catalyst on Gas Composition

In order to evaluate the effectiveness of the catalysts, gas composition vs. temperature for supercritical water gasification of grape residues at the reaction temperatures 300-600°C are presented in Fig. 2. The gaseous product was composed of hydrogen, carbon monoxide, carbon dioxide, and methane as major components and ethane, ethene, propane, and propene as minors. C4- and higher hydrocarbons were not detected. The yields (the moles of gas divided by the kg of grape residues fed into the reactor) of the major gaseous products varied significantly with reactor temperature and catalyst. CO yields in all SCWG experiments were below 0.1 mol/kg grape residues and therefore they were not shown in Fig. 2. Reaction of grape residues with supercritical water within the stainless steel reactor produced a hydrogen rich gas containing carbondioxide and methane as major components and carbonmonoxide, C_2-C_4 hydrocarbons as minors.

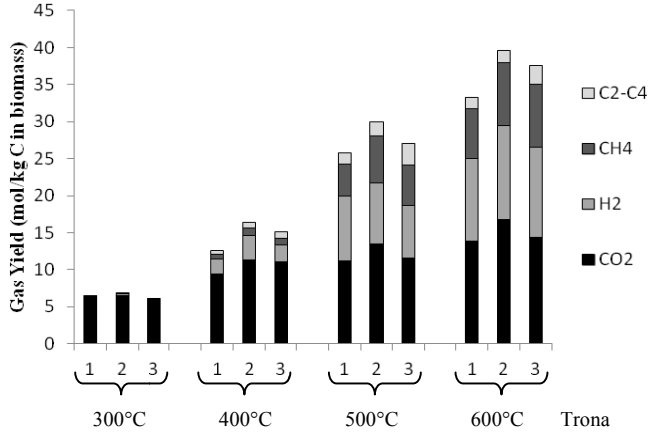


Fig. 2 Variation of gaseous product yield with temperature and catalyst for SCWG of Grape residues (1: without catalyst, 2: K_2CO_3, 3: Trona)

Catalytic supercritical water gasification lowers the activation energy for the reactions and increase the selectivity in the gas products. The results show that H_2 yield (mol H_2/kg C in grape residues) increases significantly when the catalysts are used. The catalytic effects of K_2CO_3 can be explained by catalysis water-gas shift reaction via the formate formation ($HCOO^-K^+$) [27-29].

$$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \quad (1)$$

$$KOH + CO \rightarrow HCOOK \quad (2)$$

Hydrogen is obtained by reacting of formate with water;

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \quad (3)$$

The catalytic cycle is completed by the decomposition of $KHCO_3$;

$$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2 \quad (4)$$

The overall reaction is;

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (5)$$

Methane yield increased with increasing temperature from 300°C to 600°C. Methane yield was found to be maximum at 600°C. Also the reforming of CH_4 in supercritical water was catalyzed by K_2CO_3 and Trona to the same value of 8.4 mol/kg grape residues. Carbon dioxide yield (mol CO_2/kg grape residue) increased with increasing temperature. Carbon dioxide yield was found to be maximum at 600°C in the presence of K_2CO_3. Yield of C2–C4 compounds increased with increasing temperature, also increased in the presence of trona to the highest value.

CH_4 in the product gas is produced from essentially two sources, gas phase reactions i.e. the methanation, and hydrogasification, and from reactions of organic liquid intermediates. Minowa et. al suggested that decreased H_2 production inhibited the methanation reaction by methanation of CO (Eq.(6)) and also by CO_2 (Eq.(7)) [30].

$$CO + 3H_2 \rightarrow H_2O + CH_4 \quad (6)$$

$$CO_2 + 4H_2 \rightarrow 2H_2O + CH_4 \quad (7)$$

The other important reactions as far as hydrogen production is concerned are water gas shift reaction (5), together with methane steam reforming

$$CH_4 + H_2O \rightarrow CO_2 + H_2 \quad (8)$$

For reaction temperatures of 600°C and lower, the majority of the product gas is comprised of H_2 and CO_2, also the product gas contained significant amount of CH_4. A decrease

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in the concentration of CO was observed as reaction temperature increased.

C. Effects of Temperature and Catalyst on Aqueous Product Composition

The aqueous phase contains large number of different compounds, but only key compounds like carboxylic acids (glycolic acid, formic acid, acetic acid), total furfurals (5-methyl furfural, 5-hydroxymethyl furfural, furfural,), total phenols (phenol, o-m-p cresols, resorcinol, catechol, 3-methoxycatechol, methoxybenzene and 4-methoxyphenol, 2,6 dimethoxyphenol, 2-methoxyphenol and 3-methoxyphenol, 4-methyl guaiacol, 3,4 dimethyl phenol, 3,5 dimethyl phenol and 4-vinyl guaiacol), total aldehydes and ketones (formaldehyde, acetaldehyde, acetone, propionaldehyde, 3-methyl-2-cyclo-penten-1-one, 2-cyclo-penten-1-one) were identified to interpret the effects.

Variation of aqueous product yields (g aqueous product/kg C in biomass) obtained in hydrothermal gasification of grape residues with temperature 500°C are given in Table III for experiments performed in the absence and presence of K_2CO_3, and trona.

TABLE III
VARIATION OF AQUEOUS PRODUCT YIELD IN THE ABSENCE AND PRESENCE OF CATALYST AT 500°C

Yield (g/kg C in grape residues)		No Catalyst	K_2CO_3	Trona
Total carboxylic acids	Glycolic acid	15.49	8.13	7.78
	Formic acid	12.08	6.62	5.41
	Acetic acid	14.84	11.81	6.03
Total furfurals	5-Methyl furfural	11.87	10.98	7.41
	5-Hydroxymethyl furfural	0.63	0.08	0.15
	Furfural	0.03	0.02	0.01
Total aldehyde and ketones	3-Methyl-2-cyclopentene-1-one	0.01	0.00	0.02
	2-Cyclo-pentan-1-one	0.16	0.25	0.76
	Formaldehyde	0.57	0.35	1.17
	Acetaldehyde	0.25	0.18	1.01
	Acetone and propionaldehit	4.90	6.99	15.16
Total phenols	Phenol	0.02	0.02	0.09
	m-and p-Cresols	2.64	1.08	5.23
	o-Cresol	1.75	0.10	0.39
	Resorcinol	0.17	0.12	0.96
	Catechol	0.07	0.04	0.08
	3- Methoxycatechol	0.27	0.20	0.36
	Methoxybenzene and 4- methoxyphenol	3.01	5.92	1.38
	2.6 Dimethoxy phenol	0.07	0.02	0.41
	2-Methoxyphenol and 3- methoxyphenol	0.03	0.03	0.12
	4 Methyl guaiacol	1.56	1.32	0.55
	3.4 Dimethyl phenol	0.13	0.10	0.25
	4- Vinyl guaiacol	0.37	0.34	1.56
	3.5 Dimethyl phenol	0.49	0.45	0.55
Total phenols (Colorimetric)		6.72	7.17	7.01

Aqueous product contained high concentrations of carboxylic acids such as glycolic acid. Acetic acid and formic acid which are degradation products of furfural or 5-HMF. At 500°C produced acidic intermediates glycolic, formic and acetic acid decrease by using K_2CO_3 and trona. This can be due to the formation of potassium and sodium formate salts (Fig. 3).

The simplest carboxylic acid and formic acid degradation occurs via two pathways; decarboxylation and dehydration [31,32]. The major products in gas phase CO_2 and H_2 are formed by decarboxylation of formic acid. The aqueous product includes a lot of different phenols. Ortho-. para-. meta-cresols and phenols are analyzed by HPLC and the sum of phenols is detected colorimetrically. The highest aqueous product yield was reached at 300°C in the presence of K_2CO_3. Aqueous product yield can be ordered as total carboxylic acids > total furfurals > total phenols > total aldehyde and ketones (Fig. 3).

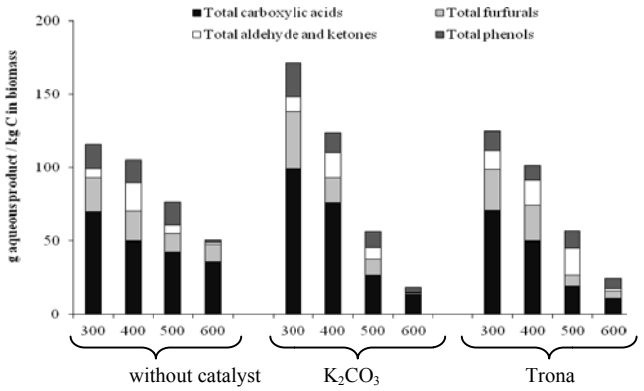


Fig. 3 Effect of temperature on aqueous product composition in the presence of K_2CO_3

The variety of the aqueous product contributes to the TOC (Total organic carbon) amount of the liquid phase. Significant differences in the TOC content are found with increasing temperature (Fig. 4). TOC value decreases with increasing temperature. As the formed aqueous products degraded into gaseous products.

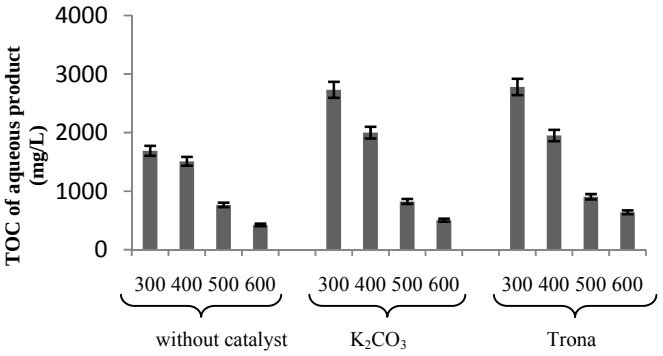


Fig. 4 Variation of TOC of aqueous products with temperature and catalyst for SCWG of grape residues

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