



Improvement in liquid fuel product quality from reactions of grape marc with CO/H₂O



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HIGHLIGHTS

- Alkali improved product quality from grape marc reaction with CO/H₂O.
- Increased reaction temperatures improved liquid fuel quality.
- Increasing temperatures gave more product hydrocarbon.
- Na₂CO₃ and NaAlO₂ lowered oxygen content in the product.

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ABSTRACT

Reactions of grape marc with CO/H₂O have been investigated over a range of temperatures (320–425 °C) with and without added sodium carbonate (Na₂CO₃) or sodium aluminate (NaAlO₂) with a view to optimising liquid fuel quality. The quality of the product can be improved by raising the temperature and/or by addition of alkali, Na₂CO₃ or NaAlO₂, which helped to decarboxylate/decompose fatty acids and lower the oxygen content. The energy recovery of the dichloromethane soluble products ranged from 50% to 75%.

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1. Introduction

As a result of rapid economic development, demand for liquid fuels is increasing much faster than supply in many parts of the world. The necessity to limit greenhouse gas emissions to prevent major undesirable climate change makes it desirable to fill the gap between supply and demand by introducing fuels from renewable sources.

Grape marc or grape pomace is the solid waste remaining after grape processing to juice or wine. It consists mainly of skin, seeds and stalks and amounts to about 20 wt.% of the grapes. In 2010, more than 67 million tons of grapes were produced world-wide, most of which were consumed fresh (~22 million tons) or processed to make wine (~36 million tons) [1]. Grape marc contains a substantial amount of crude protein, crude fiber, carbohydrate

and fatty acids [2,3], so that it is a potential renewable source of fuel.

In a previous paper we have examined the production of oil from three biomass sources (algae, grape marc and *Pinus radiata* wood chips) by thermochemical reactions under N₂ or CO/H₂O [4]. Algae were found to give significantly higher yields, but the cost of growing is high. Under CO/H₂O, yields of oil from grape marc and *Pinus radiata* were similar, but the export of *Pinus radiata* wood chips is a major industry in Australia and thus wood chips are not available in large quantities for other uses. Grape marc is available in large quantities as a by-product of the Australian wine industry, but its value-added uses are currently relatively insignificant. Compared to algae and wood chips, grape marc offers several advantages; it is cheap, it is not an important human food, the biological source is centralized and thus collection and transport costs are minimized, and its utilization can provide better ways to decrease the impact of its disposal on the environment.

Our previous work showed that the yield of oil (hexane soluble) and asphaltene (hexane insoluble) is only a crude measure of the usefulness of the product and in fact the yield of dichloromethane

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soluble material (oil + asphaltene) did not change markedly with temperature or alkali addition [4]. A product useful as a fuel should have a low heteroatom content (O,N,S) and contain a large proportion of low boiling point components, principally hydrocarbons [5]. Earlier work did not establish the characteristics of the products, therefore, in this paper the quality of the oil derived from grape marc as a function of both temperature and addition of alkali will be examined, taking into account the oil's elemental composition, proportion of different boiling point fractions and the distribution of individual compounds.

2. Materials and methods

2.1. Chemicals

CO was purchased from British Oxygen Company. Liquid chromatography grade dichloromethane (DCM), hexane (C₆H₁₄) and ethyl acetate were supplied by Merck. Sodium aluminate (NaAlO₂, technical grade) was provided by AJAX Chemicals. Sodium carbonate (Na₂CO₃, general purpose reagent) was supplied by BDH Merck. N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was provided by SUPELCO. All chemicals were used without further purification.

2.2. Preparation, characterization and reactions of grape marc

Grape marc was provided by Tarac Technologies, South Australia. The samples were collected from a number of Australian wine regions, particularly the Barossa Valley and Riverland in South Australia and Griffith (Murrumbidgee Irrigation Area) in New South Wales and were those used in the earlier study of reaction yields [4]. The seeds (ca 90%) were separated from the small amount of skins and twigs by sieving, then air-dried for 2–3 weeks and finally crushed to <1.4 mm. The moisture content, ash yield, elemental analysis and solid state ¹³C Cross-Polarization Magic Angle Spinning (CP-MAS) NMR were determined as described previously [4].

Volatile matter was determined by thermogravimetric analysis (TGA) in argon using a Setaram TAG16 Simultaneous Symmetrical Thermoanalyser. A small amount of sample (20 mg) was put in an alumina cup. The sample was heated up to 110 °C (one hour) to remove free water in the sample. Within the limits of error, the moisture content determined at the temperature used for the TGA experiment (10.9 ± 0.7%) was the same as that at 85 °C (11.1 ± 0.1%) in larger-scale moisture determination. The sample was then heated to 1000 °C at 10 °C/min in a flow of argon (70 mL/min). The temperature was held constant for 15 min at 1000 °C in a flow of argon (70 mL/min) and then for another 15 min at 1000 °C in a flow of a mixture of 10% argon/90% air (70 mL/min). The sample was finally cooled to 20 °C at 99 °C/min in a flow of argon (70 mL/min). The volatile matter of the sample was calculated from the sample weight change that occurred between 150 °C and 1000 °C in a flow of argon, relative to the dry mass. Fixed carbon was then calculated from the weight change after the mixture of argon/air was introduced into the system at 1000 °C. The physical and chemical characteristics of grape marc are presented in Table 1 and Fig. 1. Fig. 1 shows that polymorphs of cellulose and lignin [6,7] were present.

Representative samples of air dried grape marc were obtained using a V-shaped tumbling mixer or so called V-blender [8,9]. The samples were mixed repeatedly in the V-blender and the total material was divided into two; the process was repeated until the required amount was obtained. A representative sample of 2.1 g was charged into the autoclave. Reactions were carried under 3 MPa (cold) CO/H₂O for 1 h at 320–425 °C, in some cases with Na₂CO₃ and NaAlO₂ (0.5 mol or 1.0 mol of the metal (Na) per kg

Table 1
Physical and chemical characteristics of grape marc.^a

	Grape marc
Moisture content (wt.%)	11.1 ± 0.1
Volatile matter ^b (wt.% db)	66.3 ± 5.4
Fixed carbon ^b (wt.% db)	25.7 ± 3.0
Ash yield ^c (wt.% db)	6.72 ± 0.00
Elemental analysis	
Carbon (wt.% db)	46.2 ± 0.3
Hydrogen (wt.% db)	5.4 ± 0.3
Nitrogen (wt.% db)	2.8 ± 0.6
Sulphur (wt.% db)	<0.40
Oxygen ^d (wt.% db)	38.9 ± 1.2
Atomic H/C ratio	1.4 ± 0.1
¹³ C NMR ^e	
C _{C=O}	0.07
C _{ar}	0.37
C _{al}	0.56

^a The errors are based on the difference between duplicate determinations.

^b Determined by TGA.

^c 490 °C.

^d By difference.

^e Proportion of the total peak area.

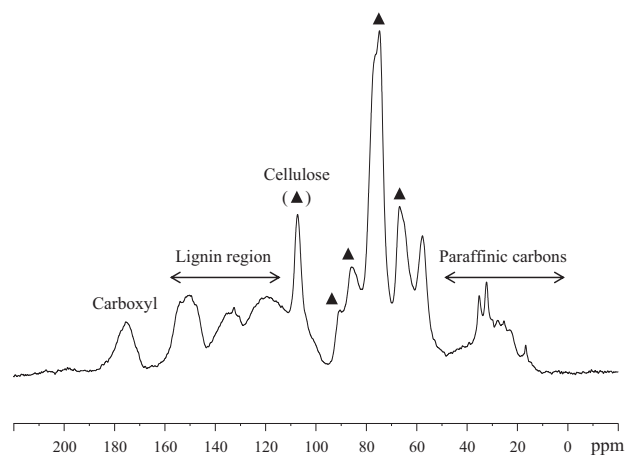


Fig. 1. ¹³C CP-MAS spectra of grape marc (▲ = cellulose derived peaks).

dry basis (db) of grape marc), in a 27 mL autoclave fitted with a stainless steel liner. The use of a small autoclave allows for a large number of reactions to be carried out in duplicate with a small amount of sample. The good reproducibility of the experiments is indicated by the low standard deviation of the duplicate results, shown in Fig. 2 as error bars. The products were separated into gas, oil (hexane soluble, DCM soluble), asphaltene (hexane insoluble, DCM soluble) and DCM insolubles, and the yields of gas, oil + H₂O and asphaltene determined as described previously [4]. The total yield of oil + water, asphaltene, and gas produced was denoted as the product yield (Eq. (1)). The difference between the product yield and the sum of the yields of all gases (including CO₂) and of asphaltene was denoted as oil + water yield (Eq. (2)). Product yield, oil + water and asphaltene yield (Eq. (3)) are presented on a dry mineral matter free (dmmf) basis, calculated from the ash yield.

$$\text{Product yield} = \left[\frac{W_{\text{charge}} - W_{\text{DCM insolubles}}}{W'_{\text{charge}}} \right] \times 100 \quad (1)$$

$$\text{Oil + water yield} = \text{Product yield} - \left[\frac{W_{\text{gas}} + W_{\text{asphaltene}}}{W'_{\text{charge}}} \right] \times 100 \quad (2)$$

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