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Sustainable options for the utilization of solid residues from wine production

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ABSTRACT

The efficient use of solid organic waste materials is an issue of particular importance for the wine industry. This paper focuses on the valorization of grape marc, the major component of winery organic waste (60–70%). Two methods were designed and compared: combustion to generate electricity, and the pyrolysis for the production of bio-char, bio-oil, and bio-gas. Each of these processes was analysed to determine their economic and environmental viability. The flow-sheeting software, ASPEN PLUS, was used to model the two cases. Data from the simulations was used to inform techno-economic and environmental analyses. Pyrolysis was found to be the superior method of utilizing grape marc from both economic and environmental perspectives. Both pyrolysis and combustion exploit the energy content of the waste, which is not recovered by the traditional treatments, composting or distillation. In addition to the production of energy, pyrolysis yielded 151 kg of bio-char and 140 kg of bio-oil per tonne of grape marc. These products may be used in place of fossil fuels, resulting in a net reduction of carbon dioxide emissions. However, the potential deleterious effects resulting from the replacement of the traditional treatments was not considered. Investment in either pyrolysis or combustion had a negligible impact on the price of the wine produced for wineries with an annual grape crush larger than 1000 tonnes. Composting has significant economic advantages in wineries with a small grape crush of less than 50 tonnes.

1. Introduction

Humans have produced wine since the dawn of agriculture during the Neolithic period over 8000 years ago (McGovern, 2007). Since then, it has become an integral part of culture, society, and religion around the world. It is therefore no surprise that grapes were one of the earliest fruits to be cultivated and are now one of the most common fruit crops in the world (Myles et al., 2011). In 2014, the worldwide production of grapes was over 77 million tonnes (Statistics Division, 2013), the vast majority of which was used for the production of 28 billion liters of wine (Wine Institute, 2011). Because of the size of this industry, and the amount of agricultural land devoted to the production of wine it is important that the environmental impact of the industry is minimized (Christ and Burritt, 2013). The recent trend towards quality-focused, small wine producers presents a challenge as it has the potential to result in decreased efficiency and an increase in the environmental impact of winemaking (Iannone et al., 2016). An important aspect of wine production that has a significant impact on the overall efficiency and environmental impact of the wine-making process is the effective minimisation, management, and utilisation of waste streams (Musee et al., 2007).

Solid organic by-products of wine production include grape marc, stalks, wine lees, and sludge. These materials are often treated as waste with little or no value. Of these materials, grape marc is the major component representing ca. 62% of the total organic waste (Ruggieri et al., 2009). Grape marc typically has a high water content (ca. 60%), but on a dry basis is comprised of skin (ca. 51%), seeds (ca. 47%) and stalks (ca. 2%) Duba, 2015. However, the specific composition of grape marc is dependent on the type of wine produced. For some grapes the proportion of stalks has been shown to be as high as 11% (Bacic, 2003). This disparity can be linked to differences in the wine production process. Red wine production often sees the stalks removed separately before the pressing process, as shown in Fig. 1. As a result, the mass of grape marc accounts for between 11% and 22% of the grapes crushed for red wine production and 12–25% for white wine production (Bacic, 2003). Another difference between white and red wine production is that red wine grape marc typically has a higher alcohol content, but lower sugar content. Such differences in composition are reflected in the ultimate analysis of grape marc. Such analyses

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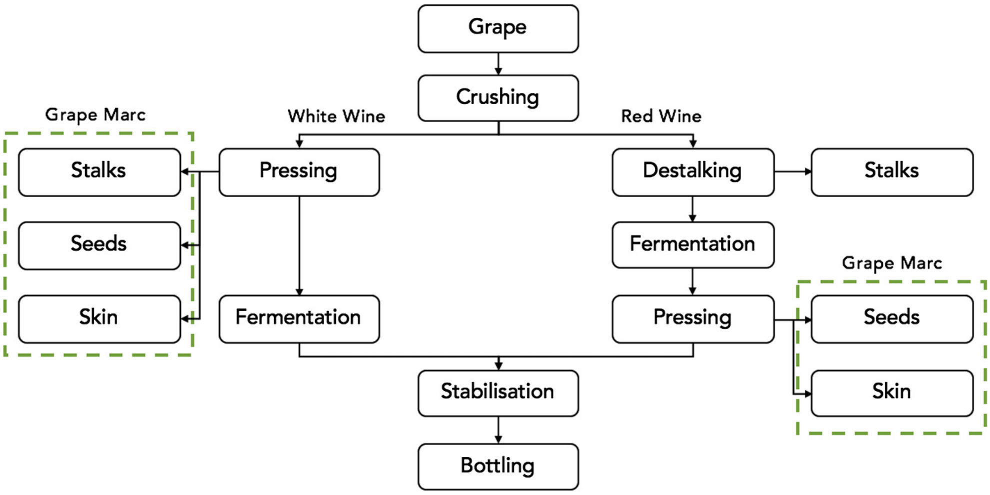

Fig. 1. Simplified wine production diagram detailing the source and composition of grape marc waste.

represent key data for the theoretical modelling of grape marc processing. However, as shown in Table 1, the ultimate analysis data from literature shows little difference in grape marc composition. Table 1 also shows ultimate analysis data from the Biomass Handbook (Hall and Kitani, 1989) which is widely accepted and used in similar studies (Domalski et al., 1986; Li et al., 2016).

In comparison to other solid hydrocarbon fuels that may be processed by either combustion or pyrolysis, such as coal, grape marc has significantly lower carbon content and higher moisture content. For example, Anthracite (a high rank coal) has moisture and carbon contents of 2.8% and 94.39%, respectively (Domalski et al., 1986). These differences are reflected in the differences in the lower heating values (LHV) of the two materials. Grape marc has as LHV of 6.00 kJ/g wb (wet bulb) (Rada and Ragazzi, 2012) and 19.14 kJ/g db (dry bulb) compared to 34.62 kJ/g for anthracite coal (Domalski et al., 1986). Due to its low energy content, grape marc is a low-grade fuel and produces a significant quantity of carbon dioxide per kilo-watt-hour (kWh) generated. However, these disadvantages are offset by the low-cost of grape marc, and because it is renewable and hence carbon neutral.

Generally speaking, the traditional treatment of grape marc includes the following methods: distillation, composting or landfill, combustion, gasification, and pyrolysis, which were summarized in Table 2. The precise distribution of grape marc handling is shown in Fig. 2 (Australian Wine Industry Association Incorporated, 2003).

Grape marc is traditionally distilled to produce grape marc spirits such as grappa (Fotakis et al., 2013). In Australia the majority of grape marc is processed by distillation. The South Australian Environmental Protection Authority (Waste Management Committee, 2001) estimated that approximately 90% of grape marc produced in South Australia undergoes distillation. However, due to a decreasing demand for the products of grape marc distillation, it has become an increasingly unattractive option for grape marc treatment. The European Council Regulation (EC) 1493/1999 on the Common Organization of the Wine Market dictates that grape marc waste must be sent to distilleries. However there is evidence that small wineries often disregard this law (Bustamante et al., 2008). Despite its wide-spread application, distillation does pose some problems. Storage of grape marc is a major concern due to the large quantities produced in a short period of time. (Faure and Deschamps, 1990) found that large quantities of stockpiled grape marc will undergo fermentation which results in the production of undesired products. Grape marc distillation produces grape marc spirits, exhausted grape marc and vinasse. Each tonne of grape marc produces approximately the same amount of exhausted grape marc, between 40 and 80 liters of spirit, and 400–1200 liters of vinasse (Newton, 2013; Larsson and Tengberg, 2014). Exhausted grape marc shares many of the disposal issues known for grape marc. Vinasse is a liquid waste product that is typically characterized by a low pH and high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Baez-Smith, 2006; Belhadj et al., 2013). These properties make vinasse a troublesome waste product which, if not treated, can cause salinization, sodification, and acidification of soil (Fuess and Garcia, 2014). Being a liquid waste product, treatment by combustion or pyrolysis is unattractive, where the pre-treatment processes required would be energy intensive and cause significant fouling (Larsson and Tengberg, 2014; Sheehan and Greenfield, 1980). Beyond distillation, the primary areas of interest for the use of grape marc is composting (Bertran et al., 2004) and feedstock (Baumgärtel et al., 2007). Other areas of research include the extraction of valuable chemicals such as polyphenols, biosurfactants, and antioxidants (Dwyer et al., 2014).

The trend towards high crop yields in agriculture has led to the exploration of a variety of organic and inorganic substrates as fertilizers. Composting offers a cheap and convenient method to treat winery waste to produce a product suitable for use as a soil conditioner. The composting of grape waste is widely studied (Ferrer et al., 2001) with consensus on the viability of the method to both manage grape marc and produce a worthwhile fertilizer (Bertran et al., 2004; Nogales et al., 2005). Composting also offers the benefit of carbon sequestration. A majority of the carbon is sequestered with a greenhouse gas (GHG) emissions of 1.31 kg

Table 1
Ultimate analysis for grape marc waste.

	C	H	O	N	Cl	S	Ash
Literature Range (Domalski et al., 1986; Li et al., 2016)	47.22–54.90	5.83–6.33	30.40–38.63	1.86–2.37	0.05	0.03–0.21	4.20–9.50
Biomass Handbook (Hall and Kitani, 1989)	52.91	5.93	30.41	1.86	0.05	0.03	8.81

Table 2
Traditional treatment methods for grape marc waste.

Methods	References	Advantages	Disadvantages
Distillation	Fotakis et al. (2013); Waste Management Committee (2001)	1. Valuable products such as grappa	1. Costly equipment – distillation column 2. Energy required for distillation 3. Only part of components recovery 4. Additional treatment required 5. Large storage scale 6. Not suitable to small vinery
Composting or Landfill	Waste Management Committee (2001), Bertran et al. (2004), Ferrer et al. (2001), Nogales et al. (2005)	1. Cheap and convenient 2. Low cost 3. Low energy required	1. Long stockpiling period 2. Soil pollution possibility 3. Waste gas emission
Combustion	Fitzgibbon et al. (1995), Navarro et al. (2000), Rada et al. (2009), Fiori and Florio (2010), Benetto et al. (2015), Cordiner et al. (2016)	1. Full waste treatment 2. Full energy recovery	1. Pre-treatment (drying) required 2. Energy required for pre-treatment
Gasification	Roos (2010)	1. Convert waste into syngas (feedstock of methanol or FT synthesis)	1. Costly equipment 2. High energy required 3. Additional feed (water, or oxygen) required 4. Profit affected by low oil prices
Pyrolysis	Chen et al. (2016), Yaman (2004), Marculescu and Ciuta (2013), Net (2012)	1. Valuable products (bio-char, bio-oil and bio-gas) 2. Simpler feeding system 3. More options for further valorisation	1. Cost of the equipment 2. Energy required 3. Pre-treatment required

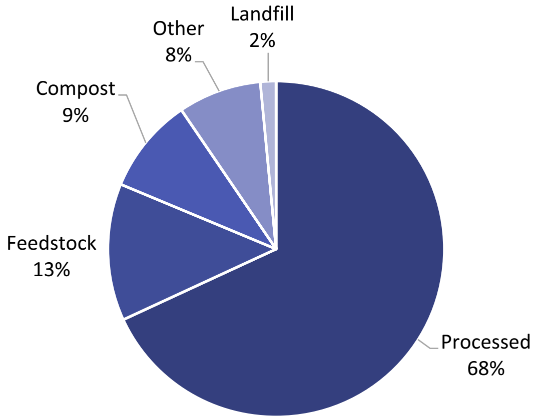

Fig. 2. The breakdown of Australian grape marc utilisation produced (Australian Wine Industry Association Incorporated, 2003).

CO2e/tonne of stockpiled grape marc over a 13-week period (Rogers, 2013). This only represents a quarter of the total stockpiling time required for grape marc. Despite the positive effects of grape marc compost on soil, the application of agricultural waste on soil may also result in heavy metal accumulation (Arvanitoyannis et al., 2008). Other concerns include the inhibition of root growth (Inbar et al., 1992) and nitrogen leaching (Bustamante et al., 2008). These concerns are tied to the long stockpiling period required to produce a usable fertilizer. Composting is often performed in an open field where it is in direct contact with the earth, and also requires proper control of temperature, moisture, and aeration to produce high quality product. Without careful monitoring of these parameters, anaerobic digestion may occur, which produces methane which has a high global warming potential compared with CO_2 emitted during well-controlled composting (Stevens and Verhé, 2004).

In the interest of sustainability, this paper investigates alternative methods for the utilisation of grape marc waste, which can be applied on-site, thereby providing a waste management method that does not require transportation and can be used by all wineries. Composting for on-site use is currently the only method that fulfils these criteria. However, despite the carbon sequestering merits of composting, the required stockpiling process is linked to a number of environmental concerns including soil and groundwater contamination as stated above. A study by Longbottom and Petrie (2015) revealed the greatest source of winery GHG emissions stem from fuel and electricity usage. Consequently, a shift toward renewable energy sources appears to be a good method for reducing GHG emissions. Furthermore, the study showed carbon sequestration as another potential opportunity to manage GHG emissions. Thermal decomposition methods (combustion, gasification, and pyrolysis) are promising alternatives that offer opportunities for carbon neutral energy production and opportunity for carbon sequestration. Unlike distillation, these alternatives do not yield further waste products or require off-site transportation.

Combustion is a process that is relied upon to produce over 90% of the world's energy, of which only 11.2% is from biomass, and thus fossil fuels (coal, oil, and gas) are the most common feedstock for combustion (Overend, 2009). The advantage of biomass over fossil fuels is its carbon neutrality; the carbon dioxide released during combustion corresponds to the carbon dioxide absorbed during photosynthesis. Combustion is described by some authors as the only method that can completely deal with the pollution potential of winery waste (Fitzgibbon et al., 1995; Navarro et al., 2000). Other advantages of biomass combustion over fossil fuels include lower sulfur and nitrogen content, low ash content, and its availability as a cheap energy source (Fernández et al., 2012).

Combustion processes using high water content feedstocks, such as grape marc, suffer from ignition issues and thus appropriate pretreatment of the feedstock is required (Rada et al., 2009). Drying is typically practiced, although this, generally reduces the overall efficiency of the process. Despite this, combustion has been shown to be an effective method for energy generation from grape marc (Fiori and Florio, 2010; Benetto et al., 2015), including electricity generation (Cordiner et al., 2016).

Pyrolysis and gasification are two alternatives to combustion that also merit consideration. Gasification involves the production of synthesis gas (or syngas) from a carbonaceous fuel in an oxygen-deficient environment. Gasification is usually performed at high temperatures, typically between 800 and 1200 °C (Roos, 2010). Syngas is a vital intermediate used in the manufacture of many chemicals, the largest applications being the production of ammonia and methanol. Despite the potential utility of syngas, the equipment requirement for processing syngas gas is likely to be impractical for winery scale operations.

Pyrolysis offers an alternative to both gasification and combustion, particularly in the wine industry. Pyrolysis involves the thermal decomposition of biomass in the absence of oxygen to produce bio-char, bio-oil, and bio-gas (Chen et al., 2016), and can be represented by the generic reaction as shown below.

$$C_aH_bO_c \rightarrow \sum_{\text{liquid}} C_lH_mO_n + \sum_{\text{gas}} C_xH_yO_z + H_2O + C \quad (1)$$

The precise yield of each product is dependent on the biomass feedstock, pyrolysis temperature, and the residence time under the pyrolysis (Yaman, 2004). Fast pyrolysis is characterized by short residence times whereas conventional pyrolysis is characterized by longer residence times. A study by Marculescu and Ciuta (2013) showed that using conventional pyrolysis of grape marc at temperatures above 500 °C, bio-gas was the main product. The lower operating temperature of pyrolysis offers an advantage over gasification due to lower CAPEX, more valuable products (bio-char and bio-oil), and simpler feeding systems without introduction of oxygen or water (Bioenergy Net, 2012).

The heat of pyrolysis is an important factor in considering the viability of a pyrolysis system. A high heat of pyrolysis will require significant energy input which may effect the profitability of the process. Despite being a popular subject of research, there is no consensus on the heat of pyrolysis for biomass. Published figures range from significantly endothermic (750 J/g) to significantly exothermic (−1700 J/g) (Roberts, 1971; Park, 2008). This large range is caused by the mixture of both endothermic and exothermic reactions that occur during pyrolysis. Typically, hemicellulose and lignin pyrolysis are exothermic reactions whereas cellulose pyrolysis is endothermic (Basu, 2013). The small amount of cellulose in grape marc compared to hemicellulose and lignin (Gómez-Brandón et al., 2011) suggest that grape marc pyrolysis is not significantly endothermic and hence would not require significant energy input. A study by Marculescu and Ciuta (2013) found that the calorific analysis of all pyrolysis products yielded a positive process energy balance at all process temperatures with 550 °C yielding the greatest overall calorific value in the products. They also concluded that the bio-gas alone was sufficient to sustain the energy requirements of the pyrolysis process. Despite significant energy being available in the products of pyrolysis, in order to extract the energy from all products, multiple energy generation methods must be employed thereby introducing additional costs and complexity. Alternatively, a fast pyrolysis may be employed to yield large amounts of bio-oil (around 80% yield), and bio-gas in a negligible quantity (Onay and Kockar, 2003). However due to its high water content, bio-oil has unfavourable ignition properties and is not an effective fuel for combustion. Furthermore, bio-oil contains highly corrosive compounds (Yaman, 2004) which can damage machinery.

The products of pyrolysis offer many options for further valorisation. Steam reforming is a viable method of upgrading the bio-oil to syngas (Chen et al., 2016; Efika et al., 2012). The combination of fast pyrolysis and steam reforming can produce a large yield of syngas as well as bio-char. The use of bio-char at wineries as a soil additive has been documented (Rosas et al., 2015) and has displayed effective results. Furthermore, the application of bio-char on soil has significant carbon sequestration potential. The conversion of biomass into bio-char results in the stable, long-term sequestration of just below 50% of the initial carbon. In comparison decomposition or composting of crop residues has a long-term carbon sequestration of ~10% of the initial carbon (Compost Victoria, 2010; Lehmann et al., 2006). Syngas is a flexible product due to the multitude of options available for its use. Potential applications of syngas include electricity generation, production of ammonia, or Fischer-Tropsch (FT) fuels. The specific use of the syngas may be influenced by the characteristics of the syngas produced as different end products have differing requirements of the syngas properties (Göransson et al., 2011). The development of a FT process incurs a risk as the product value is tied to global fuel prices (Dry, 2002). Alternatively, the value of power generation lies in the electricity offset by that generated and recycled back into the winery or distillery process. Any excess electricity can be sold for further value.

The application of pyrolysis for the utilisation of grape marc offers many potential opportunities. Despite the potentially lucrative products from processes such as steam reforming and Fischer-Tropsch synthesis, these processes, much like gasification, introduce complexity and expense. The most effective method of biomass valorisation from pyrolysis whilst still maintaining a simple and cost-effective setup would be in maximising the yield of bio-char and bio-oil. Bio-char has proven to be a useful as a soil additive and bio-oil is shown to be a competitive substitute of heavy and light fuel oils (Bradley, 2006). Pyrolysis of grape marc at 500 °C yields the highest amount of solid and liquid pyrolysis products (Marculescu and Ciuta, 2013).

Research into the use of grape marc waste as biomass for pyrolysis is deficient and hence this study focused on the realisability of the technology as opposed to real world viability.

The wine industry produces significant amounts of waste each year. The methods currently in-place are not suitable for all applications. This paper investigates the options of combustion and pyrolysis of wine production residues for their economic and environmental viability. Furthermore, the methods will be compared with current literature on wine production residue utilisation to provide an evidence-based option for a more energy effective, profitable, and environmentally friendly usage of winery waste. This study was designed to test the proposition that there are alternative methods available for managing wine production residues which provide greater economic and environmental value than currently employed methods.

2. Methodology

The generation and analysis of data were performed in three sections. A steady-state simulation of both pyrolysis and combustion processes was performed using the mass and energy balance capabilities of ASPEN PLUS (v8.4). A techno-economic analysis was performed on the results from these simulations to assess the economic viability. An environmental analysis was also performed based on the modelling results.

2.1. Modelling approach

ASPEN PLUS process modelling software was used in the investigation of pyrolysis and combustion of winery waste residues. Literature references were used to aid in the development of the process flow diagrams and operating conditions. Both processes were modelled using the Redlich-Kwong (RK) Aspen equation of state, as suggested in Abdelouahed (Abdelouahed et al., 2012) with a basis of 1 kg/s of wet biomass feed. This feed basis was then scaled for both the economic and environmental assessments for specific winery sizes.

2.2. Model description

Simplified block diagrams of the combustion and pyrolysis processes are shown in Figs. 3 and 4. The complete ASPEN PLUS flowsheets and executable files can be found in Supplementary materials. The executable ASPEN PLUS files include the detailed compositions of all components, and the thermodynamic properties applied.

2.2.1. Combustion process

Grape marc biomass enters the dryer at 60% moisture and leaves at 10% moisture. The dry biomass is combusted in a boiler to produce superheated steam at 20 bar with 138 °C of superheating. The boiler design includes an economiser, evaporator, and superheater. The combustion exhaust is recycled through the dryer to satisfy the evaporation duty. The superheated steam enters a turbine where electricity is produced before being condensed against ambient air. The water is then pumped back into the boiler at 20 bar, via the economiser.

2.2.2. Pyrolysis process

Similarly, grape marc biomass enters the dryer at 60% moisture and leaves at 10% moisture. The dry grape marc is pyrolysed at 500 °C to produce solid, liquid, and gaseous products. The products are separated. The bio-gas is combusted to generate heat and exhaust. The heat is used to supply the pyrolysis process and the exhaust is sent to the dryer to dry the grape marc biomass.

2.3. Component characterisation

Biomass, char, and ash are modelled as nonconventional solids based on their proximate and ultimate analysis as found in the literature. The HCJ1Boie method was used for enthalpy calculations and the DCOALIGT method was used for density calculations (Abdelouahed et al., 2012). Bio-oil contains a complex mixture of many chemicals which presents challenges for modelling. A simplified model was used where the bio-oil was represented as a mixture of phenol, acetic acid, and 1-hexene. The selection of these chemicals was based on the quantities in which they occur in bio-oil and representation of similar compounds found in bio-oil (Bertero et al., 2012), and simplicity in the modelling process. Similarly, bio-gas is a mix of several compounds. Bio-gas modelling was simplified as the four most common compounds found in bio-gas: carbon dioxide, carbon monoxide, hydrogen, and methane.

2.4. Process block design

2.4.1. Dryer

Dryer operations were modelled as a STOIC reactor that converted the moisture content of the biomass into a separate water component. The dryer was followed by a separator block that separated the dryer gas from the dried biomass. The moisture content remaining in the dry biomass was set by a FORTRAN calculator block.

2.4.2. Pyrolysis

Pyrolysis of the biomass was modelled as two separate processes: a decomposition block broke down the biomass into its elemental components, and a pyrolysis process which produced the pyrolysis products. Both processes were modelled using a YIELD reactor. A FORTRAN calculator block determined the C, O_2, N_2, H_2, and H_2O decomposition yields based on the proximate and ultimate analyses of the feed stream. Proximate and ultimate analyses are sourced from literature (Hall and Kitani, 1989). Pyrolysis product yield was based on literature data (Marculescu and Ciuta, 2013). Excel calculations were used to bring the yields close to literature data whilst still maintaining atomic and mass balance. The yields of char and gas products were calculated to match the literature values on the basis of mass yield. An inverse matrix method was then used to solve the component yield of bio-oil to account for the remaining atom and mass imbalance.

2.4.3. Combustion

Combustion processes are modelled as STOIC reactors. It was assumed that all combustible feed was completely combusted. That is,

$$C_aH_bO_c + \left(a + \frac{b}{4} - \frac{c}{2}\right)\mathrm{O}_2 \rightarrow a\mathrm{CO}_2 + \frac{b}{2}\mathrm{H}_2O \tag{2}$$

Excess air used for combustion reactions were set to 25% excess to mimic real world requirements for complete combustion of biomass.

2.4.4. Boiler

The boiler was modelled as four separate components: combustor to combust the biomass and generate energy, economiser to heat water to the boiling temperature, boiler to evaporate the water, and a superheater to superheat the steam. The water flow rate and exhaust temperature were adjusted to achieve maximum turbine output and an appropriate exhaust temperature for biomass drying.

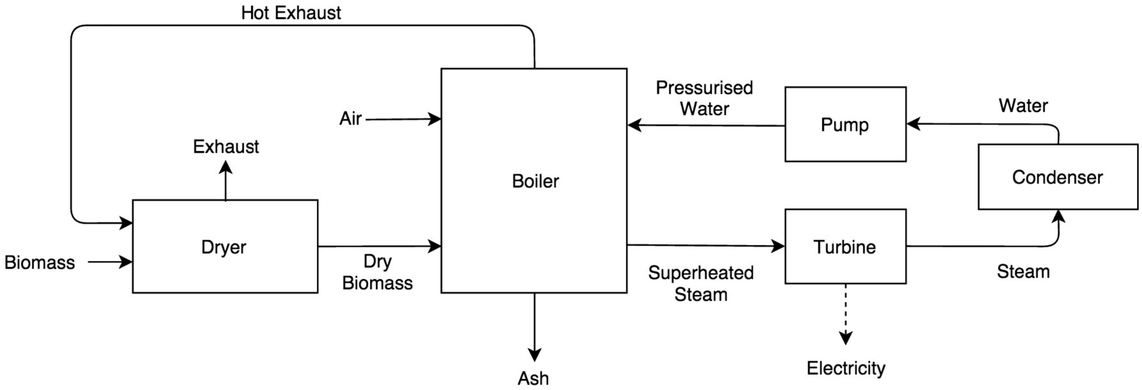

Fig. 3. Block diagram of the combustion process modelled in ASPEN PLUS.

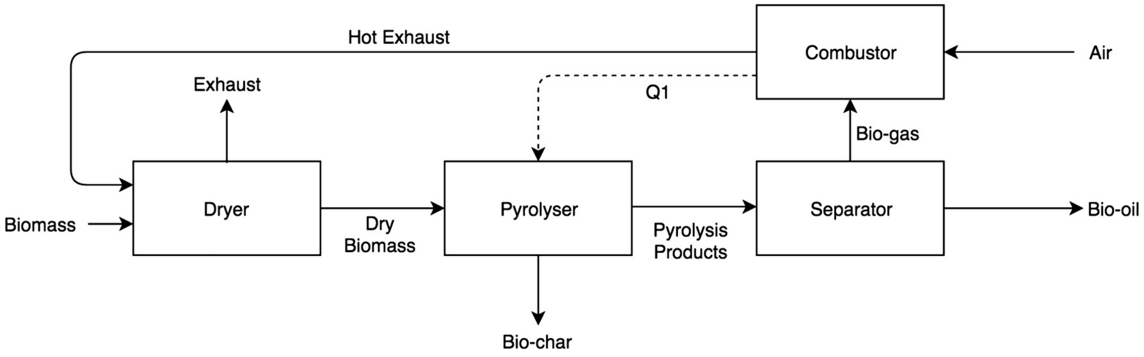

Fig. 4. Block diagram of the pyrolysis process modelled in ASPEN PLUS.

2.5. Model scaling

In order to conductance analysis of process viability for different sized wineries, wineries were categorised by annual grape crush as shown in Table 3. Results from the ASPEN PLUS simulation were given for a basis of 1 kg/s of grape marc and were scaled by the grape marc flow rates given in Table 3. The grape marc flow rate was calculated assuming operation for 12 h per day, weekdays only for four months per year to match the major harvesting period of a winery.

2.6. Techno-economic analysis

The techno-economic analysis involved evaluation of the return on investment (ROI) and overall impact on the price of wine. This required the consideration of costs, savings, and revenue streams over an investment period of 10 years. Capital costs were estimated via the exponential method with data from Perry's Chemical Engineering handbook (Green and Perry, 2008) and cross-checked via cost curves from Chemical Engineering Economics (Garrett, 1989). Total calculated capital costs were calculated by Eq. (2) below.

$$C_{total} = C \cdot f_L \cdot \left(\frac{q_2}{q_1}\right)^n \cdot \frac{CEPCI_2}{CEPCI_1} \cdot \frac{AUD}{USD} \tag{3}$$

where C is the cost, f_L is Lang factor, q is the capacity, n is a scaling exponent, and CEPCI is the chemical engineering plant cost indext. For the data not available, stimates were made via analoguous or similar process equipment. The metrics used for economic analysis are summarized in Table 4.

Revenue was calculated using the market prices for products or analoguous products. The average Australian wholesale value of electricity with the addition of environmental and policy costs (15.2 ¢/kW h) was used for economic analysis in this report. This aligns with the estimate (15 ¢/kW h) used by the Australian Wine Research institute.(Wine Institute, 2011) All values are given in 2016 Australian dollars (AUD). All market prices are based on Australian markets. The Market Prices used in the techno-economic analysis are listed in Table 5.

The overall impact on the price of wine was calculated by the following equation for the total operating term of 10 years:

$$\text{Change in Wine Price} = \frac{\text{Net Present Value Cost}}{\text{Discounted volume of wine produced}} \tag{4}$$

The net present value cost (NPV_{cost}) was calculated as (Investopedia, 2016a):

$$NPV_{cost} = \sum_t \frac{C_t}{(1+r)^t} - C_0 \tag{5}$$

where C_t is the net cash inflow during the period of t years; C_0 is the total initial investment cost; r is the discount rate which refers to the interest rate used to determine the present value of cash flows within t years (Investopedia, 2016b), and t is the number of time periods (10 years in this paper). Similarly, the volume of wine is also discounted by considering the discount rate over t years because the same present cash flow will produce more wine in the future.

$$NPV_{V-wine} = \sum_t \frac{V_t}{(1+r)^t} \tag{6}$$

Table 4
Metrics used for the technoeconomic analysis.

Operation length	10 Years
Investment term	10 Years
Construction period	1 Year
Investment interest rate	10%
Operating costs	5% of fixed capital
Depreciation	10% of fixed capital
Discount rate	10%

Table 5
Market values and prices used for the techno-economic analysis.

Product	Price
Bio-char (Jirka and Tomlinson, 2014)	\$200/tonne
Bio-oil	\$320/tonne
Electricity	15.2 ¢/kW h
Waste handling costs (Waste Management Committee, 2001)	\$0–\$60 per tonne

Table 3
Breakdown of Australian winery sizes.

Grape crush tonnes	Total wine L	Grape marc produced tonnes	Marc flow rate kg/s	Number of wineries (Nordestgaard et al., 2012)
<50	17,500	6	0.0016	1427
50–1000	367,500	116	0.0334	790
1000–10,000	3,850,000	1210	0.3501	93
10,000–20,000	10,500,000	3300	0.9549	11

where $NPV_{V\text{-}wine}$ is the discounted volume of wine and V_t the volume of wine produced during the period of *t* years. The ratio of NPV_{cost} and $NPV_{V\text{-}wine}$ leads to the cost per liter of wine on a discounted basis.

2.7. Environmental analysis

Analysis of environmental impact was performed in terms of greenhouse gas emissions given as a CO_2 equivalence (CO_2e). The complete combustion of grape marc biomass is assumed to have no net CO_2 emissions. The CO_2 emissions of other processes are adjusted accordingly to allow for consistent analysis. The CO_2 emissions offset by the use of combustion and pyrolysis processes and products were also taken into account.

3. Results

3.1. Model results

3.1.1. Combustion

Unlike pyrolysis, the combustion process was not modelled against any particular experimental data as the combustion reaction is a comparatively straight if complete combustion is ensured. Validation of the simulated model was undertaken by the comparison with other biomass-to-electricity combustion systems. A general value for biomass is 1 kW h/kg which corresponds to wood chips with a LHV of 18 kJ/g. This equates to a 20% efficiency (McKendry, 2002).

Table 6 shows the literature lower heating values (LHV) for both wet and dry grape marc and the calculated available energy density based on the final output from the combustion process. Wet grape marc shows a lower energy density as is expected. However the overall efficiency is greater than that of the dry grape marc. This is due to the inclusion of a drying process that increased the LHV by 219% whilst only decreasing mass by 55%. The precise amount of energy produced per kilogram of biomass is highly dependent on the biomass itself. A general value for biomass is 1 kWh/kg which corresponds to wood chips with a LHV of 18 kJ/g (McKendry, 2002). This equates to a 20% efficiency. The simulated results fall a little short of this value, but may be accounted for by the nature of the biomass studied.

3.1.2. Pyrolysis

Pyrolysis was validated against the experimental data for grape marc pyrolysis as performed by Marculescu and Ciuta (2013). Whilst several of the input parameters were modified to match experimental data, some results and properties of product streams cannot be controlled. Table 7 shows the modelled and experimental results for several significant values.

From Table 7, it is evident that the experimental mass fraction of products were successfully reproduced in ASPEN PLUS within a small margin of error. However, the higher heating values (HHV) of the products display a much greater variation from experimental data. This can be attributed to the simplification of both the bio-gas and bio-oil composition for modelling in ASPEN PLUS. This may suggest errors in the overall energy balance of the pyrolysis system. As ASPEN PLUS is unable to calculate the HHV for unconventional solids, the simulated HHV for the grape marc and bio-char could not be determined, thus it is difficult to draw any conclusions about the accuracy of this result. However, the HHV for grape marc exiting the decomposer in its elemental constituents had a HHV of 25.2 kJ/g. This is 32% higher than the reported HHV for dry grape marc of 19.14 kJ/g. When considering the simulated heat of pyrolysis of 365 J/g, the result falls within the range of experimental data (between −1700 and 750 J/g) and the expectation of a moderately endothermic process. Moreover, when considering the worst case scenario of a heat of pyrolysis at the most endothermic literature value, at most, the simulated result is 50% of the real value. This would require twice as much energy as simulated. However, the simulated results show the bio-gas combustion exhaust had the capacity to provide more energy to the pyrolysis. In addition, the simulated HHV for bio-gas was 24.4% lower than the experimental value and in reality would produce more energy than simulated. Therefore, in spite of the margins of error present in the energy flow simulation, the results are not expected to be detrimentally affected as a consequence.

3.2. Techno-economic analysis

The annual cash flow for both combustion and pyrolysis processes are shown in Fig. 5. Across all winery sizes, pyrolysis requires a significantly lower capital cost, approximately 50% of the cost of combustion. This can be attributed to differences in process complexity and therefore differences in the process equipment required. The major process equipment required for pyrolysis include a dryer, a pyrolysis reactor, a gas-liquid separator, and a gas combustion reactor. The only equipment of significant cost is the pyrolyser estimated at $200,000 for a 10,000–20,000 tonne grape crush winery. In comparison, the combustion process requires a dryer and a steam cycle. The components of a steam cycle are a source of substantial expense. The turbine alone for a 10,000–20,000 tonne grape crush winery was estimated to be $330,000. These capital cost calculations were performed as an order of magnitude estimate and hence are expected to have an error of 10–50% (Green and Perry, 2008). Despite this margin of error, the comparative cost between pyrolysis and combustion are as expected and are useful for preliminary analysis of the economics of the two processes.

4. Discussion

4.1. Economic benefits

Fig. 5 shows the annual capital and operating costs in comparison to the revenue from pyrolysis products and potential savings. Small wineries with a grape crush under 50 tonnes show the insignificance of the potential revenue and savings in comparison to the cost of the capital investment. However, as the size of the winery increases, the potential revenue and savings increase in comparison to the investment costs. Pyrolysis is seen to result in a net positive cash flow for wineries with a grape crush over 1000 tonnes. Similarly, combustion approaches, but never reaches, the break-even point in wineries with an annual grape crush over 10,000 tonnes. The positive relationship between winery size and cash flow can be explained by the typically non-linear relationship

Table 6
Wet and dry grape marc LHV values from literature and the energy density and efficiency as calculated from simulation results.

	LHV kJ/g	Energy density kW h/kg feed	Energy density kJ/g	Efficiency %
Wet grape marc	6.00	0.33	1.20	20
Dry grape marc	19.14	0.75	2.70	14

Table 7
Comparison of simulated and experimental mass fraction yield and HHV of pyrolysis products.

Product	Mass Fraction		% Error	HHV (kJ/g)		% Error
	Model	Experimental		Model	Experimental	
Char	0.340	0.333	1.5	n/a	27	n/a
Oil	0.315	0.333	−6.1	18.9	23	−17.8
Gas	0.345	0.333	4.6	6.8	9	−24.4

Fig. 5. Annual cash flow for investment in combustion and pyrolysis at each winery scale.

between equipment cost and processing capacity. This relationship is also reflected in the return on investment as shown in Fig. 6.

Fig. 6 demonstrates the effect of changes in product and electricity prices on the ROI. The effect is more pronounced in large-scale wineries where a significant amount of product or electricity is generated. As the size of the winery becomes smaller, the capital costs become the dominant dictator of the ROI and hence fluctuations in the value of products or electricity become negligible. Pyrolysis yields a greater ROI than combustion in all investigated cases. However, only the largest wineries see a positive ROI from pyrolysis. Taking the sensitivity analysis into account, a decrease in product prices may potentially cause a negative ROI. Due to this sensitivity, it is surmised that both pyrolysis and combustion are not economically robust investments at winery scales.

It is apparent that pyrolysis is the more economically viable method for handling grape marc waste in comparison to combustion. One factor is the aforementioned difference in the required capital cost. Another factor, as seen in Fig. 6, is the greater value of products and savings that can be generated from the process. Both processes share the benefit of offsetting the cost of grape marc management otherwise required. However, the value of pyrolysis products is greater than the value of the electricity that is generated from combustion. This of course is subject to the market price of the pyrolysis products as well as electricity prices. The value of bio-char was estimated at $200/tonne. This value reflects the use of bio-char as a soil amendment. This allowed the modelling of bio-char both as a product to be sold or as a soil amendment to be used on-site which will offset the cost of purchasing additional soil additives. The true value of bio-char may range between $100/tonne to over $3000/tonne (Jirka and Tomlinson, 2014). Due to the conservative estimate for bio-char used in this study, it is unlikely that market fluctuations will cause electricity generated from grape marc to become more valuable than pyrolysis products.

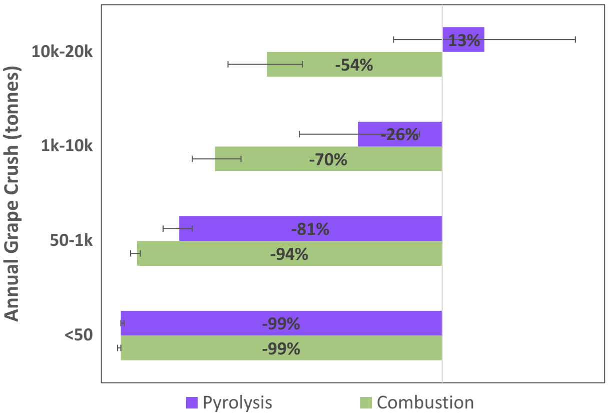

Fig. 6. ROI for combustion and Pyrolysis at each winery scale.

In order to fully understand economic impacts of these processes on the wine industry, the investment must be framed in terms of wine. Figs. 7 and 8 show how the price of wine must change in order to adjust for the profits or costs associated with the investment in either combustion or pyrolysis processes. In wineries with a grape crush larger than 1000 tonnes, the cost of treatment per liter of wine may vary from a 3¢ more to a marginal cost reduction. As a point of comparison, the average annual fluctuation in the price of grapes influences the price of wine by 10¢ per liter. Therefore, the overall effect of the implementation of combustion in wineries with a grape crush over 10,000 tonnes or pyrolysis in wineries with a grape crush over 1000 tonnes does not have a significant impact on the finances of a winery. Fig. 8 shows that this is not the case for wineries with a grape crush under 50 tonnes. Small wineries require an increase in the price of wine between $1.70 and $2.64. Consequently, investment costs

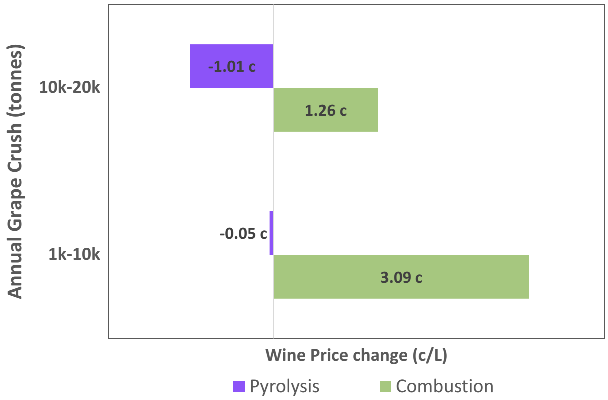

Fig. 7. Change in wine price required to mitigate the cost or profits from investment in combustion or pyrolysis for winery sizes 1000–10,000 and 10,000–20,000 tonnes/a.

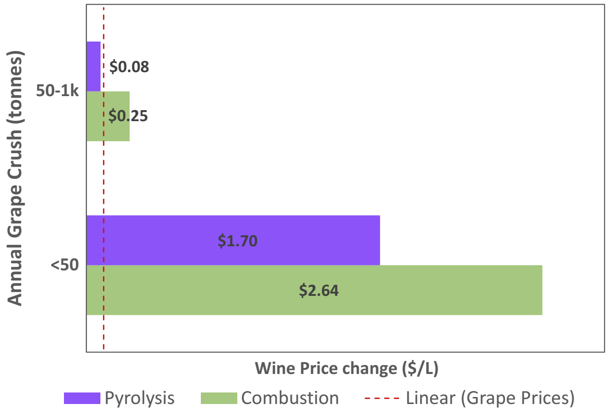

Fig. 8. Change in wine price required to mitigate the cost or profits from investment in combustion or pyrolysis for winery sizes <50 and 50–1000 tonnes/a. The average influence of annual fluctuations in grape prices is shown in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cannot be realistically mitigated by changing the price of wine in small wineries.

4.2. Environmental analysis

4.2.1. Greenhouse gas emissions

The amount of CO_2 produced from the combustion process was found to be 2.33 kg/kW h of generated electricity. Table 8 shows the emission factors (EF) for each the states and territories of Australia. Victoria has the highest EF of 1.18 kg CO_2e/kW h due to the heavy reliance on brown coal for electricity generation. Conversely, Tasmania's low EF of 0.2 kg CO_2e/kW h can be attributed to the dominance of hydroelectricity as the source of electricity generation. The EF from the combustion of grape marc is an average of 331% greater than Australian state and territory grid electricity. However, as previously established, grape marc combustion is carbon neutral with an EF of zero. Beyond being carbon neutral, the use of electricity generated from grape marc offsets the use of electricity that would have otherwise been produced from fossil fuels. Consequently, this process also achieves a degree of GHG emissions offset. The magnitude of the offset will vary between locations depending on the EF of the state or territory. In Victoria, where the EF is the highest, the largest CO_2 offset is observed at 393.7 kg CO_2e/tonne of grape marc combusted. In terms of the environmental impact, Victoria is the most viable state in which to combust grape marc for the generation of electricity.

Table 8
Australian State and Territory emission factors and the CO_2 offset from using electricity generated from grape marc waste.

State	Emission factor kg CO_2 e/kW h	CO_2 offset kg CO_2 e/tonne
NSW	0.86	−286.9
Victoria	1.18	−393.7
Queensland	0.81	−270.3
South Australia	0.61	−203.5
Western Australia	0.76	−253.6
Tasmania	0.02	−6.7
Northern Territory	0.68	−226.9

Table 9 shows the comparative emissions from the three cases: composting, combustion, and pyrolysis. Combustion results in the greatest release of greenhouse gases, followed by pyrolysis. Despite the large amount of CO_2 offset by combustion in Victoria, Table 9 shows composting and pyrolysis to be 100% and 86% more effective respectively. The effectiveness of composting and pyrolysis increases further when considering other states and territories. This conforms to expectations when considering the amount of grape marc that undergoes reactions that produce GHGs. Combustion involves the complete conversion of all carbon into CO_2 whereas a significant portion of the carbon from pyrolysis is found in either the bio-char or bio-oil products. These products, however, may still produce CO_2 depending on how they are used. The emissions given in Table 9 are scope 1 emissions (direct emissions produced on-site at the winery) and do not account for emissions from the use of the pyrolysis products. The techno-economic analysis modelled bio-char as a soil amendment and bio-oil as bunker oil. Maintaining these assumptions for the environmental analysis results in no additional CO_2 produced from the pyrolysis process. The combustion of bio-oil, as well as bio-gas, is a carbon neutral combustion process due to the renewable grape marc feedstock from which it is produced. Additionally, the use of bio-oil as bunker oil will result in the offsetting of bunker oil produced from non-renewable sources. Much like the electricity generated from grape marc combustion, the bio-oil will be partially offsetting the release of CO_2. As for the bio-char, use as a soil amendment sequesters the carbon in the soil and hence provides an opportunity to reduce the amount of GHGs in the atmosphere. Therefore, whilst scope 2 and 3 emissions are not considered, their inclusion would not be expected to cause drastic changes to the results observed in Table 9.

4.2.2. Total waste production

The environmental concerns of grape marc waste are its potential impacts on soil and land. Whilst composting typically only releases small amounts of methane, the prolonged stockpiling requirement does not address the issue of the dangers inherent in grape marc waste. Until the required stockpiling time has been reached, the grape marc still harbours the potential to negatively impact the environment. Furthermore, the 12-month stockpiling requirement for grape marc, along with the yearly harvest and pro-

Table 9
GHG emissions and adjusted emissions for composting, combustion, and pyrolysis.

Utilisation method	CO_2 equivalent emissions kg CO_2 e/tonne	Adjusted emissions kg CO_2 e/tonne
Composting	1.3	−774.8
Combustion	776.1	0
Pyrolysis	142.1	−664.0

duction of wine means wineries will also have to manage the inventory of grape marc waste over this 12 month period.

Distillation in comparison produces significantly more waste products of concern. Approximately the same amount of exhausted grape marc is produced from the fresh grape marc that is distilled, thereby extracting valuable product without reducing the quantity of waste. Moreover, each tonne of distilled grape marc will also produce between 400 and 1200 l of vinasse as shown in Table 10. Vinasse is a significantly more harmful waste product with fewer treatment options than grape marc. Ultimately distillation exacerbates the waste issue rather than ameliorates it.

From this simulation, combustion produces 776 kg of CO_2 and 35 kg of ash per tonne of grape marc. In lieu of landfill, there are several potential options for the utilisation of ash including use as aggregate in road construction or cement (Obenberger and Supancic, 2009). The most practical option available to wineries is the use of ash as a fertiliser applied directly to the vineyards. The major environmental concern of this method is the accumulation of heavy metals in the soil. However, the optimum application rate of ash ($\sim$25 tonnes/ha) is several orders of magnitude greater than the amount of ash produced $\sim$60 tonnes/ha (Yunusa et al., 2006). Due to the small amounts the ash is produced in, application of the ash as fertiliser is unlikely to be a source of major environmental concern. The 776 kg of CO_2 produced from combustion is less than the $\sim$1 tonne of stockpiled grape marc via composting resulting in an overall smaller mass of waste. However, the overall impact of stockpiled grape marc and GHG emissions cannot be directly compared on a per mass basis. GHG emissions are well studied and its environmental impact is straightforward. Conversely, the impact of stockpiled grape marc depends greatly on factors such as aeration, storage, and temperature. Properly composted grape marc may have no environmental impact whereas mishandled grape marc may produce significant quantities of methane with the resultant environmental consequence.

Pyrolysis appears to have the greatest potential for minimising environmental harm via the reduction of the overall amount of polluting mass. Like combustion, it only produces CO_2 as a waste product, however it does so at significantly lower levels.

4.2.3. Energy exploitation

Both composting and distillation extract value from grape marc waste via nutrients for plant growth and alcohol, respectively. These methods do not exploit the energy potential of grape marc waste. Whilst the LHV is low at only 6 kJ/g for wet grape marc and hence is an inefficient source of energy, the great quantities it is produced in and availability at no cost suggest that it may be a worthwhile option. Combustion and pyrolysis explore this possibility.

Combustion produces 0.33 MW h/tonne of grape marc. Pyrolysis on the other hand produces 151.1 kg of bio-char and 139.8 kg of bio-oil per tonne of grape marc with HHVs of 27 and 23 kJ/g. The bio-oil alone has an energy capacity of 0.89 MW h/tonne of grape marc. To achieve the same output as the combustion process, the bio-oil must be utilised with an efficiency of 37%. Such efficiencies are achievable and typical of oil to electricity power plants (EURELECTRIC and VGB, 2003). The use of these products as sources of energy will result in the potential offset of a significant amount of energy produced from fossil fuels with carbon neutral energy.

5. Conclusion

A review of literature and current practices revealed a lack of sustainable utilisation of grape marc waste produced on wineries. Only composting, which accounts for 9% of Australian grape marc utilisation, presents itself as a potentially sustainable option. This study looked at two alternative methods, combustion and pyrolysis.

Pyrolysis was the only case to yield a positive ROI of 13% in wineries with an annual grape crush between 10,000 and 20,000 tonnes. At all winery sizes pyrolysis yielded a more favourable ROI than combustion. The cause of this was determined to be a combination of the capital costs as well as potential savings and revenue streams for the two processes. Pyrolysis displayed higher potential value whilst maintaining a consistently lower capital cost. The steam turbine required in the combustion process is expensive and the major cause of the large capital cost requirements of combustion. In considering the investment in the context of the winery business, it was found that the profits or losses due to investment are largely negligible in large wineries. In wineries with a grape crush greater than 1000 tonnes, the overall effect on the price of wine was between -1.01 and +3.09 cents per liter. In comparison, annual fluctuations in grape prices correlate to a 10-cent change in wine price. Combustion of grape marc was found to release the largest amount of GHGs. Both pyrolysis and composting only released a fraction of the GHG produced from combustion. Composting offered the largest CO_2e abatement opportunity with a capacity of 774.8 kg CO_2e/tonne of grape marc composted. Despite the GHG emissions of combustion, the electricity generated offsets fossil fuel derived electricity with an effective CO_2e abatement with a capacity between 6.7 and 393.7 kg CO_2e/tonne of grape marc. Analysis of the material and energy transformations indicates that both combustion and pyrolysis make better use of the energy content of grape marc waste and overall produce a lower amount of waste. Pyrolysis of grape marc produced the least amount of potentially polluting material at 142.1 kg of CO_2 per tonne of grape marc. Combustion and composting produced similar amount of waste matter, however due to the extremely different nature of the waste, direct comparison is difficult. Both combustion and pyrolysis realised similar levels of energy exploitation of grape marc that neither distillation nor composting achieve.

The results of this study demonstrate that both combustion and pyrolysis are effective means to reduce the total amount of waste produced at a winery depending on the scale of the winery. Pyrolysis exhibits the greatest opportunity of waste minimisation out of all the current methods and alternative cases studied except for the

Table 10
Notable outputs from alternative and current methods used in the management of grape marc waste.

Output	Combustion	Pyrolysis	Composting	Distillation
CO_2 (kg)	776.1	142.1		
Ash (kg)	35.3			
Bio-char (kg)		151.1		
Bio-oil (kg)		139.8		
Compost (tonne)			1.0	
Exhausted grape marc (tonne)				1.0
Grape marc spirits (L)				40.0–80.0
Vinasse (L)				400.0–1200.0

energy benefit by producing 151.1 kg of bio-char and 139.8 kg of bio-oil per tonne of grape marc. The use of these products as sources of energy will result in the potential offset of a significant amount of energy produced from fossil fuels with a carbon neutral energy source. Pyrolysis is also shown to be more economically viable than combustion and has a negligible investment cost in wineries with a grape crush larger than 50 tonne annually. For smaller wineries, composting is still the most viable method for grape marc utilisation.

The context and results of this work are only examples chosen from many potential routes. Alternative methods for grape marc utilisation, beyond combustion and pyrolysis, may also be fruitful avenues of investigation due to significant variation in the requirements of different wineries, such as differences in size, location, price of feedstocks and products, etc.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2017.01.006.

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