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Effect of Hydrodistillation on 1,8-Cineole Extraction from Mallee Leaf and the Fuel Properties of Spent Biomass

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ABSTRACT: Many mallee eucalyptus species have leaves that contain terpenoid oils commonly known as eucalyptus oil, of which 1,8-cineole is the major constituent. 1,8-Cineole is potentially a high-value product that might improve the economic viability of a mallee-based biomass industry. It can be extracted by hydrodistillation, but the extraction process may affect the fuel properties of spent biomass. It was found that extraction of 1,8-cineole from mallee biomass is fast initially and tapers off to completion after 30 min of hydrodistillation. The distillation process has little effect on the fuel chemistry or the mass energy density of the spent biomass. However, hydrodistillation can potentially extract a substantial proportion of the alkali and alkaline earth metallic species from the raw biomass, depending on the biomass component (leaf, wood, and bark). Typically, Na and K are easily extracted while Mg and Ca are hard to extract. After hydrodistillation, the spent leaf becomes more difficult to grind than the raw leaf, apparently because of the poorer grindability of the oil gland enclosures and vascular bundles after hydrodistillation. However, hydrodistillation appears to have little effect on the grindability of spent wood and bark fractions.

INTRODUCTION

In southern Australian dryland agricultural regions the conversion from the original deep rooted perennial native woodlands to shallow-rooted annual agricultural species has caused extensive dryland salinity. This reflects changed water balance under agricultural systems where water is able to infiltrate below the shallow agricultural rooting depth to invigorate groundwater systems and mobilize salt stored in the subsoil. This is a serious problem especially in the southwest of Western Australia (WA) where salt damage due to shallow saline groundwater has degraded 10% of the state's 18 million hectares of agricultural land.^{1,2} It is predicted that the land area loss could increase to over 30% in the next few decades unless remedial treatments are widely adopted.^{2,3} A key strategy for combating dryland salinity is to restore a proportion of deep rooted tree cover to help deplete the surplus water accumulating in groundwater systems. Native mallee eucalypt species are being developed for this purpose.^{4–6} Mallee is planted in widely spaced narrow belts (called alley farming) to increase the effectiveness of capture of surplus water which also helps achieve higher biomass yields to improve economic performance. The proportion of area occupied by belts will usually be less than 10%.⁴

A key feature of mallee is that harvest can remove all above-ground biomass, but the retained root system can resprout or coppice to grow the next crop. This cycle of harvest and coppice can be a short 3–5 years and proceed for many decades.^{7,8} It is estimated that the potential production of mallee biomass in Western Australia alone can be up to 10 million dry tonnes per year.^{5,6} Alley farming with mallee may therefore have economic benefit through biomass production as well as being complementary to the existing agriculture. It offers the potential for a commercially viable modification to the conventional agriculture

to help remedy its serious sustainability and environmental problems at little cost.

Mallee biomass is a potential large-volume, low-cost resource for commercial uses.⁶ Its high-cineole eucalyptus oil has traditional small volume markets in various fragrance and pharmaceutical applications.⁹ However, the scale of mallee biomass production envisaged will require large volume markets and possible areas of product development include industrial solvents and bioplastics.^{10,11} Key mallee species, such as *E. polybractea* used in this study, are amenable to rapid genetic improvement to increase their concentration of leaf oil and its proportion of 1,8-cineole (averaging ~85%).¹² After oil extraction the spent biomass has potential high-volume applications for wood products and bioenergy. Another source of revenue for mallee crops may emerge with the formal imposition of limits on carbon emissions in the Australian economy.¹³

Hydrodistillation and steam distillation are commonly used essential oil extraction techniques in industry because of the high oil quality produced. Distillation can be used in either batch or semi-continuous configuration, being environmentally friendly and also relatively safe to operate compared to other processes.^{14–19} Recent progress has been made in understanding the production, economics, and carbon/energy footprints of mallee biomass as a second-generation bioenergy feedstock.^{5–8,13,20,21} On the processing side there has also been progress in utilization strategies and conversion technologies.^{13,21–28} However, one aspect of development that has

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not been addressed in any detail is impact of the eucalyptus oil distillation process on the fuel properties of the mallee biomass. Knowledge of such changes may be important to the utilization of the spent biomass in energy and fuels applications.

Traditional methods of eucalyptus oil extraction have generally been applied to whole biomass harvested either by hand or with flail type machinery both of which leave the biomass more or less in the form of intact whole stems/branches.²⁹ Development of large scale industrial biomass production has focused on a harvester designed to fell and chip the trees in a continuous action. The principle is to adapt selected tree harvesting technologies to the broad agricultural harvesting strategy seen in forage harvesting and sugar cane row crop harvesting. In a single machine and a single pass, the crop is converted from a heterogeneous collection of whole plants into a bulk chipped product that has a relatively high bulk density and acceptable handling characteristics.³⁰ Note that the chipper action has been designed to avoid any substantial leaf damage.

While it would be possible to segregate the biomass into its constituents (wood chip, leaf, and bark) this is not essential and subjecting it to hydrodistillation is also an option. Therefore, it is also desirable to obtain data and knowledge to understand the effect of hydrodistillation on the fuel properties of spent biomass from other fractions such as wood and bark.

Hence the objective of this study is to carry out a set of fundamental studies to examine the effect of hydrodistillation on eucalyptus oil extraction and on the fuel properties of the components of spent biomass. Experiments were conducted to test the performance of hydrodistillation: in extracting eucalyptus oil as a function of distillation time; in change of biomass weight, physical structure, fuel chemistry, retention of inherent ash species, and biomass grindability; and on the fuel properties of the wood and bark components.

EXPERIMENTAL SECTION

Materials and Experiments. Whole mallee trees (*E. polybractea*) were harvested from the Narrogin region in the wheat-belt area of Western Australia and then separated into leaf, bark, wood, and twig components. The biomass components were then dried in an oven (40 °C) to reduce the moisture content to ~5%. Whole leaf samples were used in subsequent hydrodistillation experiments for eucalyptus oil extraction. For wood and bark components, samples were prepared with a size of approximately 1 cm × 1 cm × 0.3 mm (length × width × thickness).

The prepared biomass samples were then subjected to hydrodistillation. In one experiment, about 10 g of biomass was hydrodistilled in 500 mL of water using a quartz beaker on a hot plate. The biomass was prepared for hydrodistillation by bringing the water to boiling point on a hot plate in a quartz beaker filled with Millipore water and covered with quartz glass. The biomass sample was then charged into the quartz beaker to start the hydrodistillation. It is important to use a low biomass loading in distillation (10 g of biomass per 500 mL of water in this study) so that upon being charged into the beaker, the biomass can be rapidly heated up to the distillation temperature. In this experiment, each individual biomass component (leaf, wood, or bark) was hydrodistilled separately, and the spent biomass samples were collected at a series of hydrodistillation times (5, 10, 15, 30, and 60 min). As twigs are fundamentally combinations of wood and bark, distillation experiments using twigs were not carried out in this study.

Table 1. Properties of Mallee Leaf, Wood, and Bark Biomass Samples

sample	leaf	wood	bark
cineole, % db	5.3	n.d.	n.d.
moisture, % (ad)	4.9	4.2	6.4
proximate analysis, % db			
ash	5.0	0.5	6.8
volatile matter	75.2	82.8	72.8
fixed carbon	19.8	16.7	20.4
ultimate analysis, % daf			
C	53.2	48.5	44.3
H	6.6	6.1	6.6
N	1.33	0.22	0.41
S	0.13	0.03	0.07
Cl	0.28	0.05	0.30
O ^a	38.46	45.1	43.69
contents of inorganic species in biomass, wt % db			
AAEM species (analyzed by IC)			
Na	0.508	0.020	0.158
K	0.392	0.101	0.259
Mg	0.129	0.077	0.218
Ca	1.604	0.111	4.760
Other inorganic species (analyzed by ICP-AES)			
Si	0.0417	0.0053	0.0634
Al	0.0211	0.0032	0.0023
Ba	0.0013	0.0004	0.0009
Fe	0.0175	0.0002	0.0015
P	0.0896	0.0167	0.0312
Sr	0.0066	0.0018	0.0162
Ti	0.0005	0.0001	0.0003

^a By difference; n.d.: not detected; ad: air-dried; db: dry basis; daf: dry ash free; IC: ion chromatography; ICP-AES: Inductively coupled plasma atomic emission spectroscopy.

Quantification of 1,8-Cineole in the Raw and Spent Leaf Samples. Solvent extraction was used to remove essential oil compounds and water for subsequent analysis. Biomass samples of approximately 3 g were weighed and boiled under reflux for 3 h in 50 mL of ethanol containing 0.25% methyl isobutyl ketone (MIBK). Any loss of weight after this process was adjusted by adding fresh solvent before analysis. The concentration of cineole was determined using a Hewlett-Packard 5890 gas chromatograph fitted with a split injector, flame ionization detector and Alltech AT-35 capillary column, 60 m × 0.25 mm i.d. × 0.25 μm film thickness. The carrier gas was hydrogen, flowing at approximately 1 mL/min, the split ratio was 50:1, and the injection volume 10 μL. Peaks were recorded and processed using DELTA (Dataworx, Brisbane) software. For each extract the area of the cineole peak was compared with that of both the internal standard (MIBK) and four external standards injected in duplicate. The water content of the ethanol extracts was determined by the Karl Fisher method. Weighed aliquots of 25 μL of solution were titrated using a Metrohm 756 KF Coulometer attached to a 774 Oven Sample Processor. The water content was used in calculation of the cineole content of the biomass samples expressed as a percentage of dry weight.

Fuel Properties and Characterization of Raw and Spent Biomass. The proximate analysis of raw and spent mallee biomass samples was done following a standard procedure. Fuel chemistry of the raw and spent biomass was determined via ultimate analysis using a series of analytical techniques. C, H, and N were analyzed using an Elemental Analyzer according to Australian Standard AS1038.6.4. Total S and Cl contents were determined by Eschka method according to Australian Standards AS1038.6.3.1 and AS1038.8.1. Total O content was determined by difference from the C, H, N, S, and Cl contents of the sample, on a dry-ash-free (daf) basis. The calorific value of raw and spent mallee biomass samples was determined using a Leco AC350 calorimeter, according to AS 1038.5. The properties of the raw mallee leaf, wood, and bark are listed in Table 1.

Grindability, Energy Density, and Particle Structure of Raw and Spent Biomass. The raw and spent biomass samples were ground in a Retsch Mixer Mill MM400 laboratory ball mill for biomass grindability assessment. It is important to note that in this study ball milling is only used as a tool at a laboratory-scale for assessing and benchmarking the grindability of various biomass materials. Prior to grindability assessment, the whole raw or spent leaf samples were cut into approximately 1 cm × 1 cm (length × width). Various lengths of grinding time were applied, ranging from 0 to 15 min, and the ball mill was operated at a frequency of 15 Hz. The volumetric energy densities of various fuels were determined from the calorific value and bulk density of the compacted ground fuels. Cross sections of the raw and spent biomass samples were prepared and then examined using a Scanning Electron Microscope (Philips XL30) for structural characterization. To prepare the sample specimen, the dried raw and spent biomass samples were arranged longitudinally and then set in the epoxy resin which was then solidified, polished, dried in the oven (~50 °C) overnight and coated with carbon for SEM observation.

Quantification of Inorganic Species in the Raw and Spent Biomass Samples. The contents of inorganic species in various biomass samples were determined using a method specially developed for biomass and biochar analysis.²⁶ Approximately a 10 mg sample was loaded into a platinum (Pt) crucible then ashed in air, following an ashing program designed to retain all inorganic species in the ash. For the determination of alkali and alkaline earth metallic (AAEM) species, the ash sample in the Pt crucible was then acid-digested in a Teflon vial using a mixture of concentrated HF:HNO₃ (1:1) solution at 120 °C for 12 h. After the evaporation of the excessive acids, the digested sample was dissolved in 0.02 M methanesulfonic acid solution, which was then injected into a Dionex 3000 ion chromatography installed with CS12A guard and analytical columns and a thermal conductivity detector for the quantification of AAEM species. Determination of other inorganic species (Al, Ba, Fe, P, Si, Sr, and Ti) was also done for the raw biomass samples. In this case, the ash sample obtained from the ashing of raw biomass as described above underwent borate fusion. The concentration of those inorganic species in the solution was then determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The contents of inorganic species in the raw biomass are listed in Table 1.

RESULTS AND DISCUSSION

Extraction of 1,8-Cineole from Mallee Leaf and Structural Changes in Leaf during Hydrodistillation. For the leaf of mallee species (*E. polybractea*) used in this study, the eucalyptus

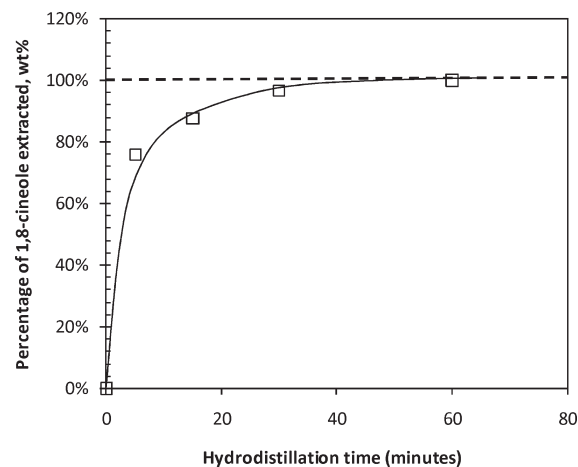


Figure 1. Extraction of 1,8-cineole from mallee leaf as a function of hydrodistillation time.

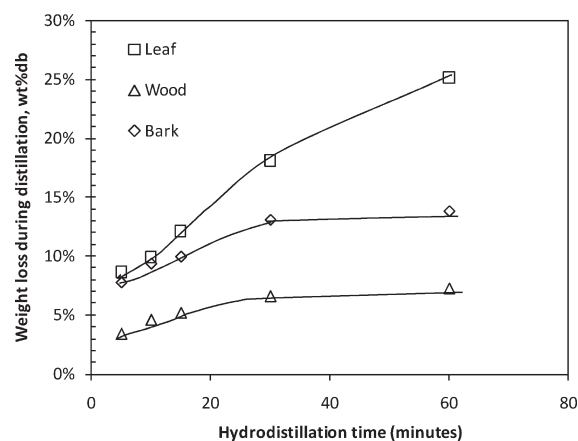


Figure 2. Loss of biomass materials during hydrodistillation of mallee leaf, wood, and bark.

oil contained 90% 1,8-cineole. Hence the study focused on the extraction of 1,8-cineole from the leaf samples. From the operational perspective it is important to understand the minimal time required to extract 1,8-cineole from leaf. Figure 1 presents the extraction of 1,8-cineole from the mallee leaf as a function of hydrodistillation time up to 60 min. Two important observations can be made from this figure. One is that extraction of 1,8-cineole is rapid initially. A 5-min period of hydrodistillation extracted ~75% of 1,8-cineole from the leaf. The other is that a minimum of 30 min was required for complete extraction of 1,8-cineole from the mallee leaf samples. A period of 30 min hydrodistillation is therefore required for completing 1,8-cineole extraction under experimental conditions in this study.

Figure 2 further presents the percentage of loss in biomass weight as a function of hydrodistillation time for mallee leaf, wood, and bark. It should be noted that all biomass components experienced some loss of biomass materials during hydrodistillation, and such losses generally increase with time. After 5 min distillation, the weight losses of leaf, wood, and bark were approximately 8, 3, and 7 wt % on a dry basis (db), respectively. The weight losses increase to 17, 6, and 12 wt % db, respectively after 30 min hydrodistillation. While further distillation resulted

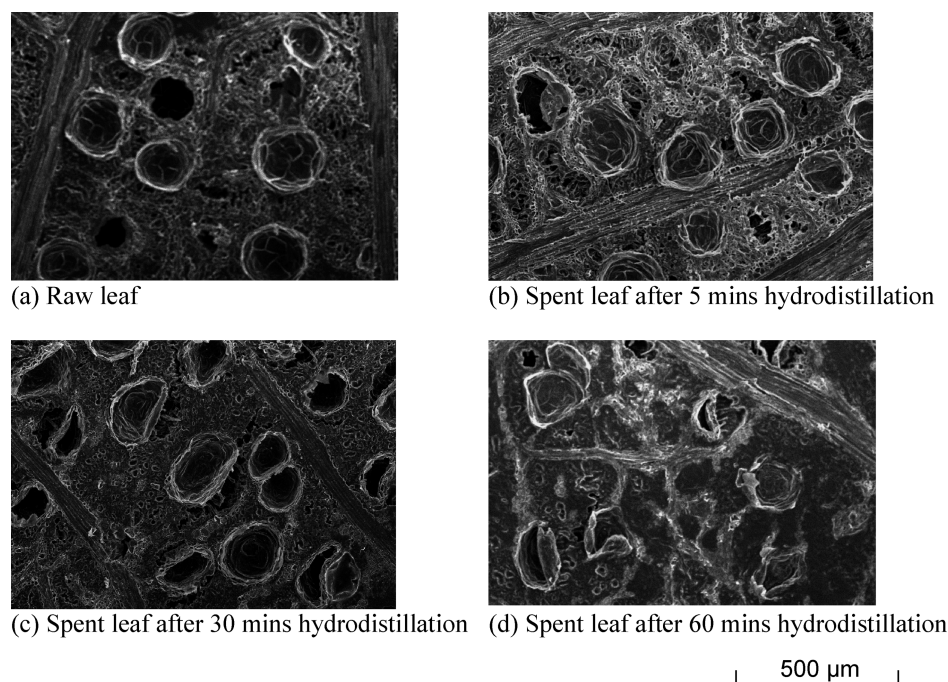


Figure 3. SEM images of the raw mallee leaf and spent mallee leaf after hydrodistillation.

Table 2. Effect of Hydrodistillation on Fuel Properties of Spent Biomass Samples

samples		proximate analysis				ultimate analysis					
		moisture	ash	volatile matter	fixed carbon	C	H	N	S	Cl	O
		(% ad)	(% db)	(% db)	(% db)	(daf)					
wood	raw	4.2	0.5	82.8	16.7	48.5	6.1	0.22	0.03	0.05	45.10
	5 ^a	4.0	0.3	83.9	15.8	48.6	6.2	0.21	0.02	0.02	44.95
	10 ^a	4.0	0.2	84.5	15.3	48.9	6.1	0.19	0.02	0.01	44.78
	15 ^a	4.3	0.2	84.7	15.1	48.7	6.1	0.22	0.02	0.01	44.95
	30 ^a	4.4	0.1	83.1	16.8	48.9	6.3	0.19	0.02	0.01	44.58
	60 ^a	4.0	0.1	85.4	14.5	48.8	6.3	0.20	0.02	0.01	44.67
leaf	raw	4.9	5.0	75.2	19.8	53.2	6.6	1.33	0.13	0.28	38.46
	5 ^a	4.3	2.5	77.7	19.8	53.2	6.6	1.43	0.13	0.23	38.41
	10 ^a	4.3	2.2	78.3	19.5	53.3	6.5	1.36	0.13	0.24	38.47
	15 ^a	4.3	2.0	78.9	19.1	54.5	6.9	1.59	0.13	0.24	36.64
	30 ^a	4.3	1.9	79.1	19.0	54.3	6.8	1.52	0.13	0.14	37.11
	60 ^a	4.2	1.9	81.1	17.0	54.4	6.9	1.68	0.12	0.12	36.78
bark	raw	6.4	6.8	72.8	20.4	44.3	5.3	0.41	0.07	0.30	49.62
	30 ^a	6.7	4.3	75.5	20.2	42.8	5.3	0.42	0.08	0.06	51.34
	60 ^a	6.5	4.2	75.9	19.9	42.6	5.3	0.44	0.08	0.04	51.54

^a Minutes hydrodistillation.

in little further weight loss for wood and bark components, there was continuous weight loss during the hydrodistillation of the leaf component. For example, after 60 min hydrodistillation, the mallee leaf experienced ~25 wt % db weight loss. As shown in Table 1, the content of 1,8-cineole in the mallee leaf is 5.3 wt % db, it is clear that a substantial amount of biomass materials were degraded and entered into the solution during hydrodistillation.

Further efforts were taken to investigate the changes in the macrostructure of leaf during hydrodistillation. As shown in Figure 3, various cross-sectional specimens were prepared from the raw and spent leaf samples and then examined under scanning electron microscope (SEM). As illustrated in Figure 3a, mallee leaf contains abundant oil glands, which are round, distributed in the leaf, and have various sizes (diameters). It is known that the leaf of *E. polybractea* (blue mallee) has

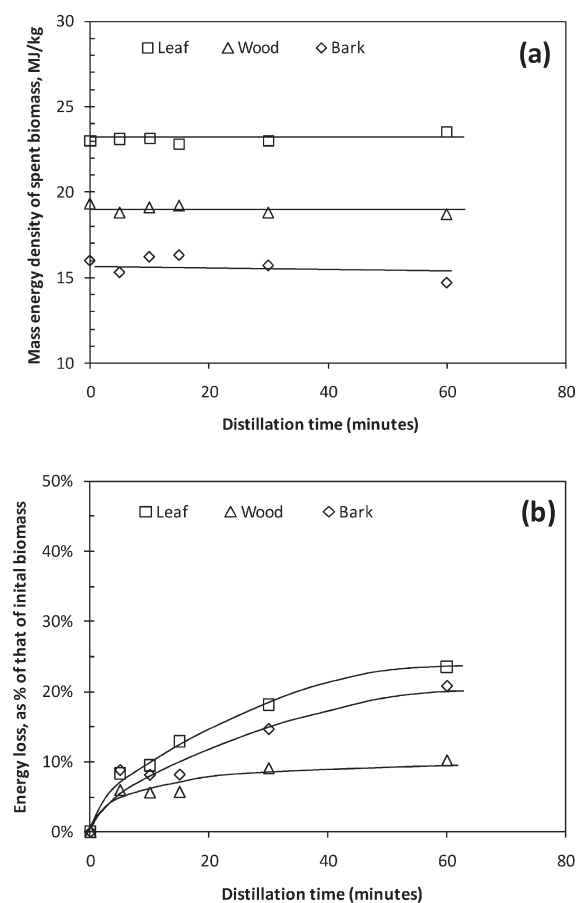


Figure 4. Mass energy density of the raw and spent biomass from mallee leaf, wood, and bark: (a) Mass energy density and (b) Energy loss after hydrodistillation.

relatively high density of oil glands (260–500 glands/cm²), and the diameters (sizes) of oil glands are also positively related with age.³¹ For the longer hydrodistillation time, Figures 3b–3d clearly demonstrate the substantial changes in leaf structures as results of the interactions between leaf and water during the hydrodistillation process. The anatomy of mallee leaf consists of a superficial layer of epidermal cells with photosynthetically active mesophyll cells densely packed just below the epidermis with more loosely packed or spongy within the leaf. Networks of vascular bundles are the paths for entry of water and nutrients and despatch of photosynthates. Oil glands lie just below the epidermis and are derived from epidermal tissue.^{9,29} Figure 3b shows that even a 5 min period of hydrodistillation appears to degrade at least part of the biomass in the leaf structure. As shown in Figure 3b, there are more large pores present in the cross-section of the leaf structure, near the enclosures of the oil glands, that appears to be disintegration of the components such as spongy mesophyll cells. Given the initially very rapid extraction of 1,8-cineole (see Figure 1) it is likely that at least part of the walls of oil glands may have degraded to facilitate oil release. However, the oil gland enclosures and vascular bundles within the leaf structure appear to maintain their shape. After 30 min hydrodistillation, the leaf has undergone substantial structural changes. A large proportion of the porous structures within the leaf appear to have collapsed. It is also noteworthy that the enclosures of the oil glands have experienced a large degree of

deformation and can no longer hold their round shapes but the vascular bundles still seem to maintain their structure. As shown in Figure 3d, after 60 min hydrodistillation, the leaf structure no longer has a clear texture, apart from the presence of almost completely deformed oil gland enclosures and still identifiable vascular bundles that however have also experienced at least partial degradation. Therefore, it is clear that hydrodistillation leads to the loss of at least a proportion of biomass materials and significantly affects the structure of biomass. The influence of such changes on the fuel properties of the spent biomass is discussed in the following sections.

Effect of Hydrodistillation on Fuel Chemistry and Mass Energy Density of Spent Biomass. Table 2 lists the fuel properties of the raw and spent biomass samples after various hydrodistillation periods. It is interesting to note that the hydrodistillation process appears to have no substantial effect on the fuel properties. The fuel chemistry of the raw and various spent biomass (based on elemental analysis) are largely similar, with similar C, H, N, and O contents. The data suggest that while there are significant losses of biomass materials as hydrodistillation proceeds, elemental losses are proportional to weight loss. As fuel calorific value (mass energy density) is an important consideration in biomass utilization for fuels and energy applications, further analyses were conducted to measure that mass energy density of the raw and various spent biomass materials. As shown in Figure 4a, the mass energy density of leaf, wood, and bark are ~23.0, ~19.0, and ~15.5 MJ/kg (db). Hydrodistillation seems to have little effect the fuel mass energy density, consistent with the ultimate data in Table 2 that clearly suggest hydrodistillation has little effect on fuel chemistry of the raw and spent mallee leaf, wood, and bark samples. Considering the loss of biomass materials during hydrodistillation, the net energy losses in various spent biomass materials were then calculated and presented in Figure 4b. After 30 min hydrodistillation, the net energy losses are 9.0, 14.6, and 18.1% for spent bark, wood, and leaf, respectively.

However, two important changes were observed in the fuel properties. First, from proximate analysis, the data shows that hydrodistillation leads to a substantial reduction in the ash content in the spent biomass materials, suggesting part of the ash-forming species were leached out of biomass during hydrodistillation. A 30 min hydrodistillation appears sufficient to nearly complete ash leaching from the spent biomass so that the measured ash contents reach the minimum. Second, from elemental analysis, the contents of Cl in the biomass were reduced substantially as hydrodistillation proceeds while little S was leached out. The data on Cl and S in Table 2 are in agreement with the data reported in our related study on extensive water washing of mallee biomass samples (150–250 μ m), which suggest the Cl in mallee biomass samples is mostly water-soluble (or most likely in salt forms) but S is water insoluble (or possibly in the forms of organically bound S in biomass structures).³²

Extraction of Inorganic Species in Biomass as Results of Hydrodistillation. Inherent inorganic species in biomass, particularly the AAEM species that can form low-melting-point silicates or sulphates, are known to be responsible for undesired ash related problems including sintering, agglomeration, deposition, erosion, and corrosion in various applications.^{33–38} For example, such low-melting-point ash species may result in ash deposition on heat transfer surfaces³³ or lead to defluidization in a fluidized-bed.^{34–37} Combustion of synthesis gas containing alkali vapors in gas turbine are also responsible for notorious ash

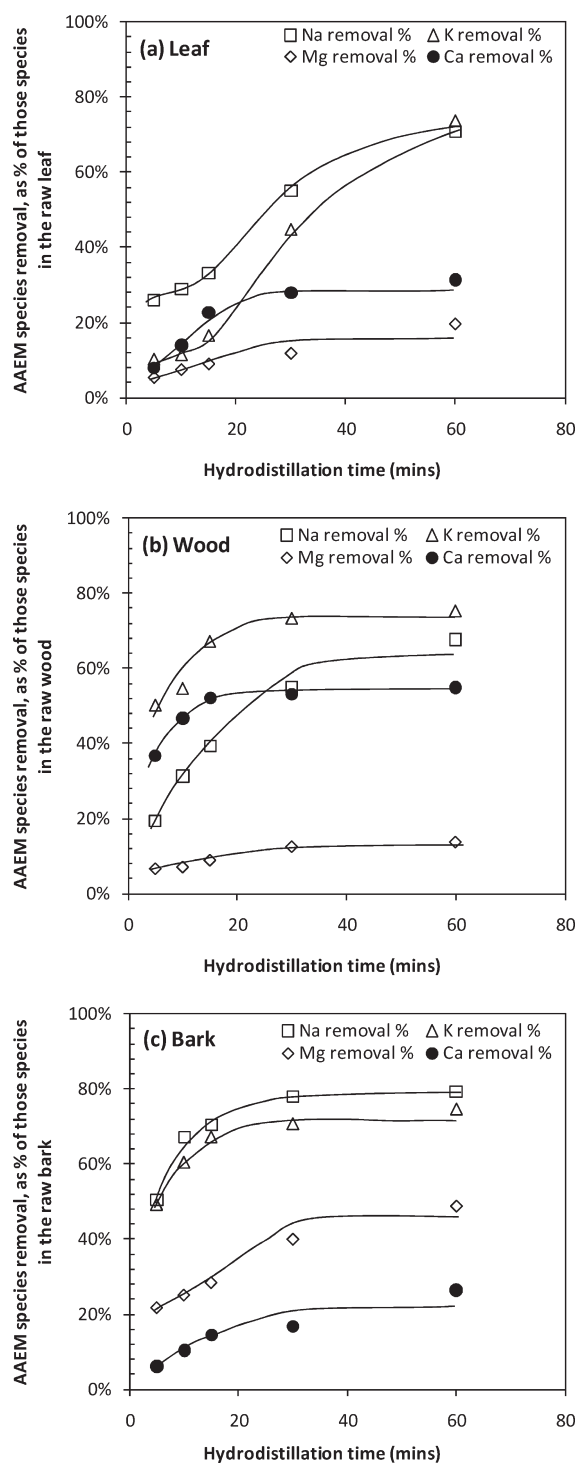


Figure 5. Extraction of Na, K, Mg, and Ca from mallee leaf, wood, and bark via hydrodistillation.

deposition, erosion, and corrosion on the turbine parts.³⁸ As shown in Table 1, AAEM species are the dominant inorganic species (>90% of the total inorganic species) present in mallee leaf, wood, and bark. Hence it is important to consider these species when mallee biomass is to be used as a fuel and this was a focus in present study.

Figure 5 presents data on the removal of AAEM species (i.e., Na, K, Mg, and Ca) in leaf, wood, and bark as a function

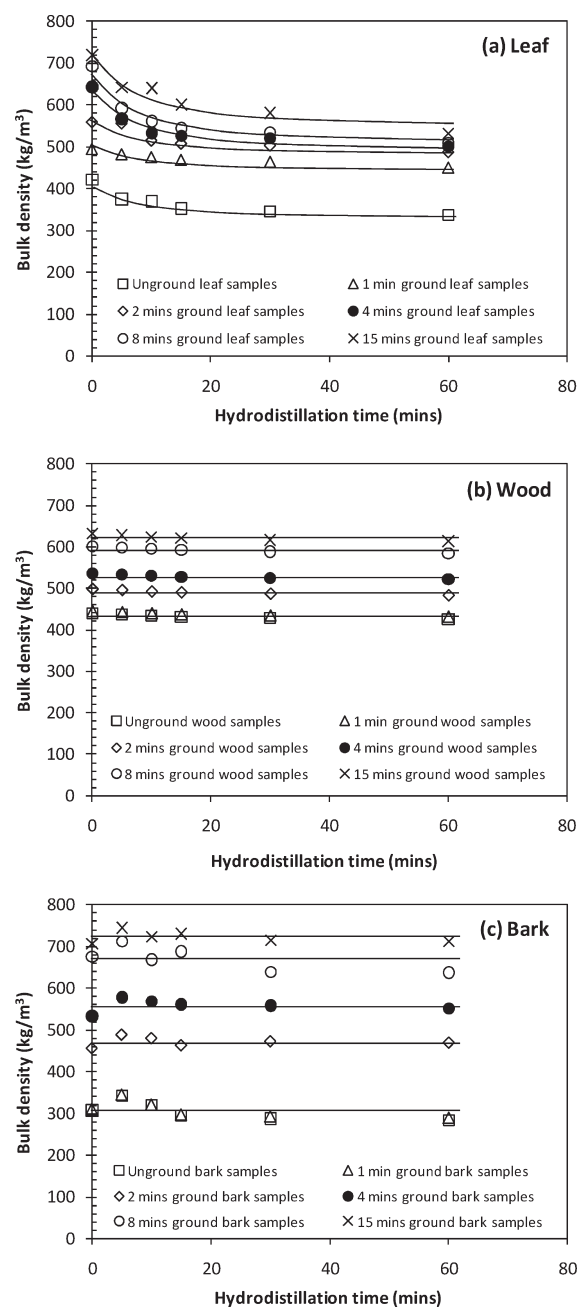


Figure 6. Grindability of the raw and spent biomass from mallee leaf, wood, and bark components.

of hydrodistillation time. Several interesting observations can be made from these data. First, for all mallee components, at least a proportion of Na, K, Mg, and Ca can be extracted via hydrodistillation. This is consistent with the fact that these species are often in water-soluble forms in mallee leaf, wood, and bark.³²

Second, the extraction of AAEM species initially increases with duration of hydrodistillation, but reaches a maximum after 30 min and then levels off. One exception is the case for Na and K in the leaf component. After initial extraction within 5 min, it showed little extraction with further hydrodistillation up to 15 min, but then exhibits a substantial increase in extraction during the 15 to 30 min period that continues to increase from

30 to 60 min of hydrodistillation. This increase in Na and K extraction after 15 min hydrodistillation appears to coincide with the increase in the loss of biomass materials in leaf component (see Figure 2) and the increase in Cl extraction (see Table 2). It appears that at least some of water-soluble Na, K, and Cl are locked in enclosed cell structures of leaf component initially and only become accessible to dissolution after a sufficient period of hydrodistillation (in this case, 15 min).

Third, the data in Figure 5 suggest that the extraction patterns of AAEM species via hydrodistillation vary from component to component. Generally speaking, Na and K are easier but Mg and Ca are relatively harder to be extracted. The majority of Na and K in mallee leaf, wood, and bark are known to be water-soluble³² and can be extracted after a sufficiently hydrodistillation period as shown in Figures 5a–c. It is also known that the majority of Mg in leaf and wood components is not water-soluble and close to 50% of Ca in wood and Mg in bark are water-soluble.³² Therefore, it is not surprising that only ~10% of Mg is extracted from leaf and wood components via hydrodistillation while the extraction of Ca from wood and Mg from bark are much higher. Table 1 shows that bark has an exceptionally high Ca content, accounting for ~4.76% of dry bark. This is probably because bark is a major storage tissue during nutrient translocation and Ca is highly accumulated and deposited in bark, via the formation of chemical bonds with acidic (e.g., carboxylic, carbonate, and phenolic) groups in bark.³⁹ Therefore, the majority of Ca in bark and leaf is not water-soluble. This is consistent with the observation that only a small proportion of Ca (~20%, see Figures 5a and 5c) was extracted from leaf and bark during hydrodistillation.

Effect of Hydrodistillation on the Grindability of Spent Biomass. Fuel grindability is also a key consideration in practical application. Generally, size reduction of biomass incurs significant energy consumption because biomass has a poor grindability related to its bulky and fibrous nature. This may limit the adoption of biomass as a fuel for co-firing in conventional coal-based power plants where ready incorporation of fine biomass is required.^{40,41} Therefore it is important to understand the effect of hydrodistillation on the grindability of spent biomass materials. In this study, a procedure is developed to assess biomass grindability indirectly. Briefly, each biomass sample had similar particle size (1 cm × 1 cm × 0.3 mm) before being subject to grinding for times ranging from 1 to 15 min. The biomass powder after grinding was then packed into a cylinder to measure bulk density.

The results are presented in Figure 6, from which several important observations can be made. First, for a given biomass sample, a longer grinding time results in a higher bulk density. This is expected because extended grinding produces finer biomass powder, leading to better packing and hence increased bulk density. Second, the raw biomass materials of various mallee components exhibit grindability in the decreasing order of bark > leaf > wood. After 15 min grinding, the bulk density increases from 300 (unground biomass) to 720 kg/m³ (ground biomass) for bark component, from 400 (unground biomass) to 700 kg/m³ (ground biomass) for leaf component and from 400 (unground biomass) to 620 kg/m³ (ground biomass) for wood component. Third, hydrodistillation appears to have little effect on the grindability of spent biomass materials from mallee wood and bark components. However, hydrodistillation reduces the grindability of spent biomass materials from mallee leaf component. For example, after 15-min grinding time, the bulk densities of leaf-derived biomass after grinding decreases from 720 kg/m³

for raw leaf component, to 620 kg/m³ for spent leaf biomass after 15 min distillation, then to 600 kg/m³ for spent biomass after 30 min distillation and further to 580 kg/m³, for spent leaf biomass after 60 min distillation. It can be seen that such a reduction in spent leaf grindability mainly develops in the first 15 min of hydrodistillation and further hydrodistillation leads to little further reduction in the grindability of the spent leaf biomass. Figure 3 shows that the major structure changes in leaf component after <30 min hydrodistillation appear to be the disintegration of the components such as spongy mesophyll cells while the oil glands and vascular bundles seem to maintain their structures. These data suggest that the grindability of spent leaf biomass is mainly limited by the poor grindability of oil glands enclosures and/or vascular bundles after hydrodistillation.

CONCLUSIONS

This study investigated the effect of hydrodistillation on 1,8-cineole extraction from mallee leaf component and the fuel properties of spent biomass. The results show that the extraction of 1,8-cineole in leaf component is fast initially and completed after 30 min hydrodistillation. The fuel chemistry and the mass energy density of the spent biomass materials prepared from the hydrodistillation of the raw mallee leaf, wood, and bark components are similar to those of the raw biomass. However, significant proportions of alkali and alkaline earth metallic species can be extracted from the raw biomass, depending on the biomass component (leaf, wood, and bark). Na and K are easily extracted but Mg and Ca are difficult to be extracted. Hydrodistillation has little effect on the grindability of spent wood and bark components but reduces the grindability of spent leaf component, apparently because of the poor grindability of oil gland enclosures and vascular bundles after distillation.

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