Formation of levoglucosenone and furfural from three different carrageenans via acid-catalyzed pyrolysis in polyethylene glycol

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ABSTRACT

To further develop the potential for carrageenan-use in a seaweed biorefinery, the acid-catalyzed pyrolysis of kappa-, iota- and lambda-carrageenans has been studied in polyethylene glycol (PEG). Using differential scanning calorimetry, it was found that decomposition temperatures for the three polysaccharides were broadened and lowered by 33–60 °C in the presence of H_2SO_4 and PEG compared to polysaccharide alone. Levoglucosenone (LGO) and furfural were the major products from all polysaccharides with LGO yields of 21.3 mg/g_{carr} (3.5 mol %), 10.7 mg/g_{carr} (2.2 mol%) and 3.9 mg/g_{carr} (1 mol%) and furfural yields of 5.9 mg/g_{carr} (1.3 mol%), 2.8 mg/g_{carr} (0.7 mol%) and 1.2 mg/g_{carr} (0.4 mol%), for kappa-, iota- and lambda-carrageenans, respectively. Total sulfate inversely correlated with the generation of volatile compounds, and the 3,6-anhydro structure may encourage the formation of the major products during the acid-catalyzed pyrolysis of carrageenan in PEG.

1. Introduction

Seaweeds are one of the most abundant sources of marine biomass and are a potential source of feedstock for the chemical industry (Wei et al., 2013; Baghel et al., 2015; Lakshmi et al., 2020). Studies on the production of fine chemicals from seaweed polysaccharides are emerging, while fine chemicals from terrestrial biomass have been widely investigated (Lichtenthaler and Peters, 2004; Corma et al., 2007; Dodds and Gross, 2007). Carbohydrates in marine and terrestrial biomass differ. Terrestrial biomass consists of unmodified hexose and pentose polymers, while marine biomass has a greater diversity of structures (Corma et al., 2007; Cosenza et al., 2017). These carbohydrate differences mean that techniques developed for terrestrial biomass valorization may not be applicable for marine derived biomass, and provides opportunities for innovative research into the conversion of abundant carbohydrates in marine biomass into novel and valuable materials.

Carrageenans have attracted intense attention among the polysaccharides in seaweeds due to their wide ranging applications in the food industry (Hotchkiss et al., 2016). Carrageenans consist of linear, sulfated galactan and are extracted from certain species of *Rhodophyta* (red seaweeds), predominantly from the species *Euchema, Gigartina,*

Chondrus crispus and *Hypnea* (Campo et al., 2009). There are three important commercial types of carrageenans, termed kappa-, iota- and lambda-carrageenan, grouped by the sulfate ester and sequence of β-(1 → 3) linked D-galactopyranose, α-(1 → 4) linked D-galactopyranose, and α-(1 → 4) linked 3,6-anhydro-D-galactopyranose residues, as shown in Fig. 1.

Pyrolysis is one approach for decomposing biomass into useful products such as bio-oil for fuels, bio-chars for energy, and platform molecules for synthesis (Zaror and Pyle, 1982; Yang et al., 2007; Babu, 2008; Bridgwater, 2012). Acid-catalyzed pyrolysis of cellulose is now used at an industrial scale for the production of levoglucosenone (LGO) and its reduced analogue Cyrene™ (CircaGroup, 2023). These compounds have applications as chiral starting materials and biorenewable solvents in the materials and pharmaceutical sector (Sarotti et al., 2012; Comba et al., 2018). The production of LGO requires solvents that are stable at the high temperatures used in the dehydration of cellulose (Cao et al., 2015). The pyrolysis of cellulose in sulfolane at 200–280 °C by Kawamoto and Saka (2007) yielded up to 42.2 mol% LGO on mg scale, and the use of tetrahydrofuran (THF) by He et al. (2017) gave LGO up to 39.5 mol% at 210 °C. These polar solvents reduce the temperature required for the production of LGO and favour its formation by the stabilization of oxocarbenium intermediates (Greatrex et al., 2017). A
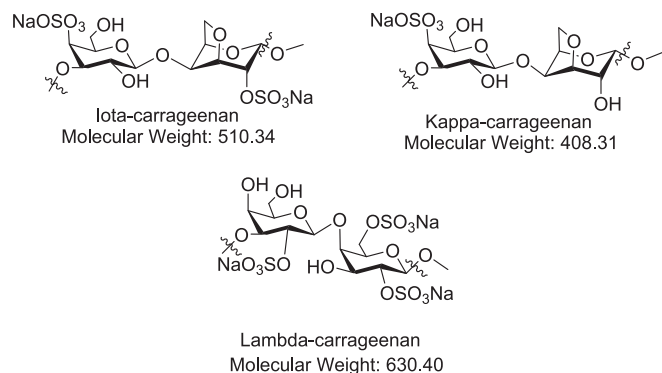

Fig. 1. Chemical structure of three different carrageenans (van de Velde et al., 2002).

recent study reported preparative yields of 18 mol% LGO from cellulose in sulfuric acid and polyethylene glycol (PEG) at 170–200 °C from cellulose (Klepp et al., 2020). Here higher loadings of carbohydrates (25 % w/w) were used compared to the conditions explored in the acid-catalyzed pyrolysis of cellulose in THF (1 % w/w) (He et al., 2017). We have recently investigated the acid-catalyzed pyrolysis of isolated iota-carrageenan in PEG, and found that LGO and furfural are the major products at 150–200 °C, although yields were low (Rodiahwati et al., 2023).

The pyrolyses of polysaccharides derived from seaweeds rich in carrageenans have been studied by a number of groups. LGO and other anhydrosugars were first reported from iota-carrageenan derived from *E. spinosum* by Helleur et al. (1985) at an analytical scale using fast pyrolysis-GC/MS at 750 °C without catalyst and solvent. Uncatalyzed pyrolysis of red seaweed *Gracilaria* in microwave-mediated experiments at 130 °C yielded bio-oils rich in aromatics, sugars, and other high-value compounds (Budarin et al., 2011). Another *Gracilaria* study under hydrothermal treatment in a dilute acid solution at 160–200 °C produced levulinic acid (16.3 wt%), which can also form from LGO under aqueous acidic conditions (Cao et al., 2019). Understanding the catalyzed pyrolysis of the various carrageenans derived from seaweeds is required to determine how the sulfate content affects the pyrolysis reaction. Thermochemical studies of the isolated carrageenans will inform the utilization of the different red seaweeds for energy and chemical feedstock production in a seaweed biorefinery.

2. Material and methods

2.1. Materials

Iota- and kappa-carrageenans were purchased from Sigma-Aldrich Co., Australia while lambda-carrageenan was purchased from The Melbourne Food Ingredient Depot. Polyethylene glycol (PEG), MW 6000-7500, was purchased from BDH Chemicals. Concentrated H_2SO_4 (95–98 %), methanol and ethyl acetate were supplied by Chem-Supply Pty. Ltd. Australia. Anthracene was used as the internal standard in the mass-spectral calibration of LGO and furfural yields. Pure anthracene and furfural were purchased from Sigma Aldrich Co. while laboratory reagent grade LGO (99.4 wt% pure) was supplied by Circa Sustainable Chemicals (Victoria, Australia).

2.2. Differential Scanning Calorimetry (DSC)

DSC experiments were conducted using a heat flux NETZSCH DSC 3500 Sirius with a liquid N_2 cooling system. Carrageen samples with and without H_2SO_4 and PEG were prepared with the same concentrations as for the preparative pyrolysis experiments. Weighed fine powder samples (5–15 mg) were placed inside a 70 µl of pierced ceramic crucible. In the furnace chamber, an empty crucible was placed next to the sample as a reference (blank). The chamber is comprised of a furnace and integrated temperature sensors, with specific locations for both sample and reference crucibles. Measurements were conducted in non-isothermal conditions over the temperature range of 25 °C to 400 °C, a heating rate of 10 K/min, and with an auto-cooling system in a N_2 environment. The temperature ranges used to analyse the evolved products during the preparative pyrolysis experiments were determined using the findings from DSC experiments.

2.3. Preparative pyrolysis experiments

The preparative-scale pyrolysis experimental procedures have been described in detail (Rodiahwati et al., 2023). PEG flakes (8.0 g) and each carrageenan (2.0 g) were mixed in a 250 ml beaker. At room temperature, methanol (1 ml) was used to dilute concentrated H_2SO_4 (0.2 g), which was then added to the PEG/carrageenan mixture. This corresponds to 2 wt% acid, which has been found to achieve maximum yields of LGO at the lowest acid concentrations from iota-carrageenan pyrolysis in PEG (Rodiahwati et al., 2023). After one to 2 min of stirring, the PEG, acid and carrageenan mixture was set aside to stand in the fume hood allowing the methanol to evaporate. The last step involved loading the final mixtures inside and in the middle of a long, horizontal glass tube (B24, 600 mm), which was attached to a receiver flask. A rotary vane oil-pump with a liquid N_2 trap was then used to evacuate the glass tube. The tube was placed in a split tube furnace with a temperature controller (Schneider Electric Eurotherm Controller model 2416). The mixtures were then heated (5 °C/min) from room temperature to a maximum temperature determined from the relevant DSC profile. The evolved products were trapped into a round-bottomed flask chilled at liquid N_2 temperatures. Any condensed material was washed from the glassware into the collection flask at the end of the reaction. The maximum temperature was held constant for a further 60 min, and GC/MS was then used to evaluate the distillate. Each pyrolysis experiment was repeated.

2.4. Gas chromatography/Mass spectrometry (GC/MS) analysis

The Agilent GC system 7890A coupled with the 5975C inert mass-selective detector (MSD) with triple-axis detectors was used for the GC/MS analysis. Samples were prepared in 2 ml clear vials with ethyl acetate as the solvent. The temperature of the column ramped from 50 °C to 250 °C over the course of 20 min. All major products evolved between 4 and 12 min. Identification of the volatile compounds was accomplished by comparison with mass spectral fragmentation patterns in the NIST mass spectra library (National Institute of Standards and Technology, Mass Spectrometry Data Center, US Secretary of Commerce, Gaithersburg, Maryland, USA, 2020). The identities of LGO and furfural were determined using authentic samples.

2.5. Quantification

Concentrations of evolved levoglucosenone (LGO) and furfural were calculated by calibration with pure compounds and an internal standard (anthracene). Response factors (RF_P), were determined from the ratio of the total ion current (TIC) in the GC/MS spectra for pure compound (A_P) to the internal standard (A_{IS}). Values of RF_P were then used to calculate product concentrations in the pyrolysate (C_p):

$$C_P(mg/ml) = \frac{A_P \; C_{IS}(mg/ml)}{A_{IS} \; RF_P} \qquad (1)$$

where, C_{IS} is the internal standard concentration in the pyrolysate. Product yields (Y_P, mg/g_{carr}) were then determined from the following equation, as previously described (Rodiahwati et al., 2023):

$$Y_P \ (mg/g_{carr}) = \frac{C_P(mg/ml) \ m_D(mg)}{\rho_D(mg/ml) \ m_{carr}(g)} \qquad (2)$$

Here, m_D and m_{carr} are the masses of the pyrolsate and carrageenan, respectively and ρ_D is the density of the pyrolsate.

Percentage molar yields (Y_P, mol%) of the products were calculated by multipying by the molar mass (MW_{carr}) of each carrageenan motif (kappa-, 204.2 g/mol; iota-, 255.2 g/mol and lambda-, 315.2 g/mol) and dividing by the molar mass ($MW_{LGO/FF}$) of the LGO (126.1 g/mol) and furfural (96.1 g/mol).

$$Y_P \ (mol\%) = \frac{Y_P \ (mg/g).MW_{carr} \ (g/mol)}{MW_{LGO/FF} \ (g/mol)} \qquad (3)$$

3. Results and discussion

3.1. Thermal decomposition of carrageenan

Differential Scanning Calorimetry (DSC) was performed to investigate the thermal decomposition behaviour of each carrageenan prior to preparative pyrolysis. The combined DSC thermograms of the three pure carrageenans from 80 °C to 280 °C are shown in Fig. 2a, while Fig. 2b-d are plots of the separated thermograms. In general, all carrageenans irrespective of sulfation pattern show a sharp, exothermic peak associated with the depolymerization of materials. This temperature corresponds to the devolatilization stage, where a range of volatile compounds evolve, resulting in a large weight loss from the polysaccharide (Ma et al., 2012).

Iota- and lambda-carrageenans showed similar exothermic peaks, at 192 °C and 191 °C, respectively. For kappa-carrageenan the analogous exothermic peak was at 233 °C. These peaks are observed at much lower temperatures than for terrestrial plants (327–370 °C) which consists of mainly unmodified glucopyranose derived polymers (Vamvuka et al., 2003). To determine the effect of total sulfur content in carrageenan on the decomposition temperature, the three polysaccharide samples were analysed by microanalysis. Although kappa-, iota and lambda-carrageenans are expected to have on average 1, 2 and 3 sulfates per repeating unit, there is expected to be natural variability in the

polysacharide, and the process involved in the isolation could affect the degree of sulfation. The total sulfur content in the iota and lambda carrageenans used in this study were found to be similar, which agrees with previous findings (Rochas et al., 1986) even though lambda has a higher theoretical degree of sulfation. Kappa-carrageenan (1 sulfate ester) had 5.6 % total sulfur while iota- (2 sulfate esters) had 10.07 % total sulfur and lambda- (3 sulfate esters) had 10.03 % total sulfur. This corresponded to 0.71, 1.48 and 1.54 sulfate units per repeating unit, respectively. The temperature required for the depolymerization to initiate correlated well with the total sulfur content and not with the presence of the 3,6-anhydro ring-system. Presumably, this is because alkylsulfate hydrolysis leads to acid formation which then catalyzes the depolymerization. A small endothermic peak at 190 °C in the DSC thermogram of kappa-carrageenan was attributed to melting and was confirmed using manual capillary melting point analysis.

The decomposition enthalpies for the principal exothermic peaks in iota-, lambda-, and kappa-carrageenan were -168, −168, and -134 J/g carrageenan, respectively. There is a weak correlation in the magnitude of the enthalpies with the degree of sulfation in the disaccharide motif. The largest decomposition enthalpy corresponded to iota-carrageenan and lambda-carrageenan with higher sulfates, while the kappa-carrageenan with lower sulfate had the smallest enthalpy. A full linkage analysis of the polysaccharides was beyond the scope of the current work.

The thermochemical behaviour of the three different carrageenans were then studied in the presence of PEG and H_2SO_4. Mixtures of carrageenan, PEG and 2 % H_2SO_4 were prepared, and the solid mixtures were then encapsulated in a ceramic pan for the DSC experiments (Fig. 3). In the presence of PEG and H_2SO_4, the primary exothermic peaks were broader, smaller, and in all instances observed at lower temperatures. The exothermic peaks for iota-, lambda-, and kappa-carrageenan were shifted to lower temperatures by 60 °C, 35 °C, and 30 °C, respectively. In these temperature regions no exothermic or endothermic processes were observed in the absence of PEG and H_2SO_4. Enthalpies of decomposition were -98, -104, and -50 J/g carrageenan for iota-, lambda-, and kappa-carrageenan, respectively. The exotherms from the pyrolysis of these mixtures were broad indicating a wide range
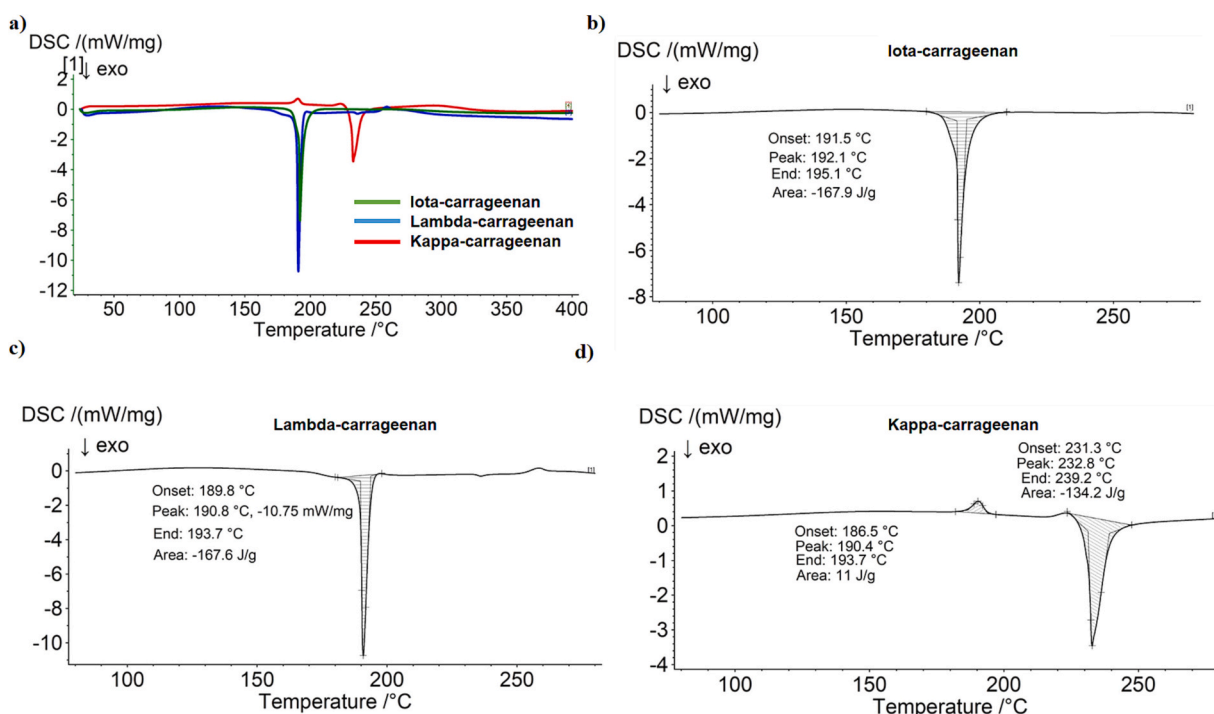

Fig. 2. DSC thermograms of different types of carrageenans (iota-, lambda- and kappa-).
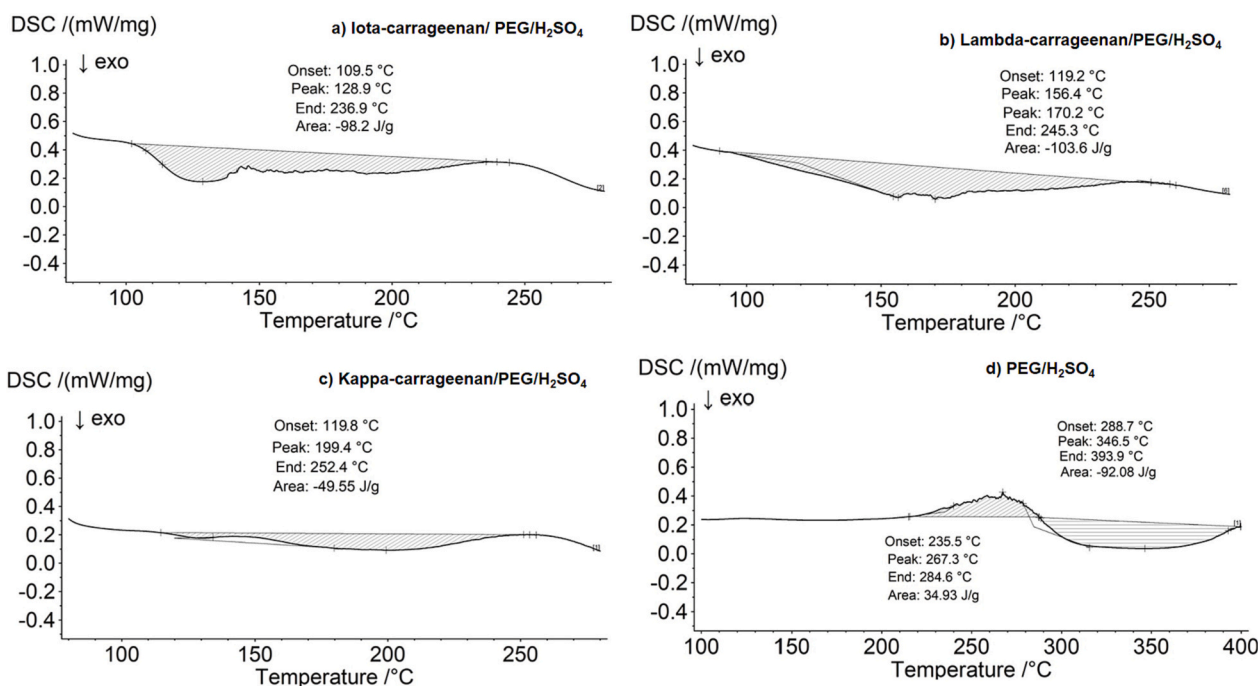
Fig. 3. DSC thermograms of three carrageenans mixed with PEG and H_2SO_4 at 80–280 °C. The PEG melting endotherm (50–80 °C) has been removed.

of reactions. Also, measured enthalpies are affected by the endothermic PEG pyrolysis at the highest temperatures (Fig. 3d). As a consequence, decomposition enthalpies cannot be readily interpreted. In solvent assisted catalyzed pyrolysis, a large difference in temperature between the reactions of substrate and solvent is required to ensure cleaner products without solvent derived impurities and to enable solvent recycling (Wang and Lakerveld, 2018). The lowering of temperatures for the DSC exothermic peaks when compared with the pure carrageenans were encouraging, due to the reduced energy requirements and the possibility of the production of valuable fine chemicals.

3.2. Acid-catalyzed pyrolysis of carrageenan in PEG

To determine the molecular characteristics of the polysaccharides that affect the product types and yields, preparative scale pyrolysis reactions of carrageenan with PEG and H_2SO_4 were performed in a tubular furnace maintained at less than 10 mbar. The maximum temperatures used for each of the pyrolysis experiments were determined from the DSC thermograms (150 °C, 200 °C, 200 °C, for iota-, lambda-, and kappa-carrageenan, respectively). Evolved products from these experiments were compared with the products from pyrolysis reactions of the carrageenans without PEG and H_2SO_4. The gas chromatograms displaying product distributions are shown in Fig. 4, and the volatile compounds are listed in Table 1 according to their elution order. Percentage peak areas are the percentage of the total ion content (TIC) for each measured product. The major acid-catalyzed pyrolysis product from all three carrageenan types was LGO, with lambda- and iota-carrageenan having the greatest selectivity. These results obtained by GC/MS were corroborated through NMR analysis of the crude distillate after removal of water.

For iota-carrageenan, LGO and furfural were the dominant pyrolysis products when the polysaccharide was heated with or without PEG and H_2SO_4 (Fig. 4 and Table 1). In the absence of PEG/H_2SO_4, reactions were more selective for LGO (18.7 % in PEG/H_2SO_4; 61.4 % for pure iota-carrageenan). Although the total quantity of volatile materials produced and the overall yield of LGO was higher for the catalyzed pyrolysis. Trace products were similar in both the catalyzed and uncatalyzed reactions, and included furyl hydroxymethyl ketone, levulinic acid, 5-

methylfurfural and 5-methyl-2(5*H*)-furanone. Additional products only observed in the presence of PEG and H_2SO_4 were methyl levulinate and dimethyl hepta-2,4-dienoate, and two considerable peaks at retention times of 10.93 mins (12.1 % of the TIC) and 11.35 mins (24 % of the TIC). These peaks could not be identified in the NIST library, and the detailed MS spectra of these compounds are listed in the Supplementary Materials.

For the lambda-carrageenan pyrolysate, distributions of products similar to the iota-carrageenan pyrolyses were observed. Uncatalyzed pyrolysis selectively produced small quantities of LGO and furfural, and under acid-catalyzed conditions there was a significant increase in the yield of LGO. Trace amounts of the ester methyl levulinate were detected, while levulinic acid found from iota-carrageenan was not observed. Greater selectivity for furyl hydroxymethyl ketone were seen in the uncatalyzed reaction (22 % of the TIC) compared to the catalyzed reaction (13 % of the TIC). The higher temperatures used in the pyrolysis compared with iota-carrageenan pyrolysis led to the formation of crown ether by-products at retention times, 8.79 min, 11.38 min and 11.48 min. These products are consistent with the DSC thermograms (Fig. 3) where decomposition is occuring at temperatures greater than 200 °C, and are associated with PEG decomposition.

For kappa-carrageenan, the percentage areas of LGO and furfural peaks and hence selectivity in both catalyzed and uncatalyzed pyrolysates were similar, however, there was a five-fold increase in the yield of LGO with acid catalysis in PEG (Table 1 and Fig. 5). A greater number of peaks were observed in the chromatograms of kappa-carrageenan chromatograms when compared with the other carrageenans. These included trace peaks that were present in only one of iota- or lambda-carrageenan. Both 2-acetylfuran and isomaltol were detected only in the pyrolysates of kappa-carrageenan. These materials are common carbohydrate pyrolysis products (Moe et al., 2022; Ito, 1977). Methyl levulinate (4.6 % of the TIC), levulinic acid (0.5 % of the TIC) and dimethyl hepta-2,4-dienoate (1.1 % of the TIC) were identified in the pyrolysate with PEG and H_2SO_4 and not the uncatalyzed reaction. Minor amounts of crown ethers were also observed at retention time 8.789 min, and is due to PEG decomposition at higher temperatures (Vitali and Masci, 1989).

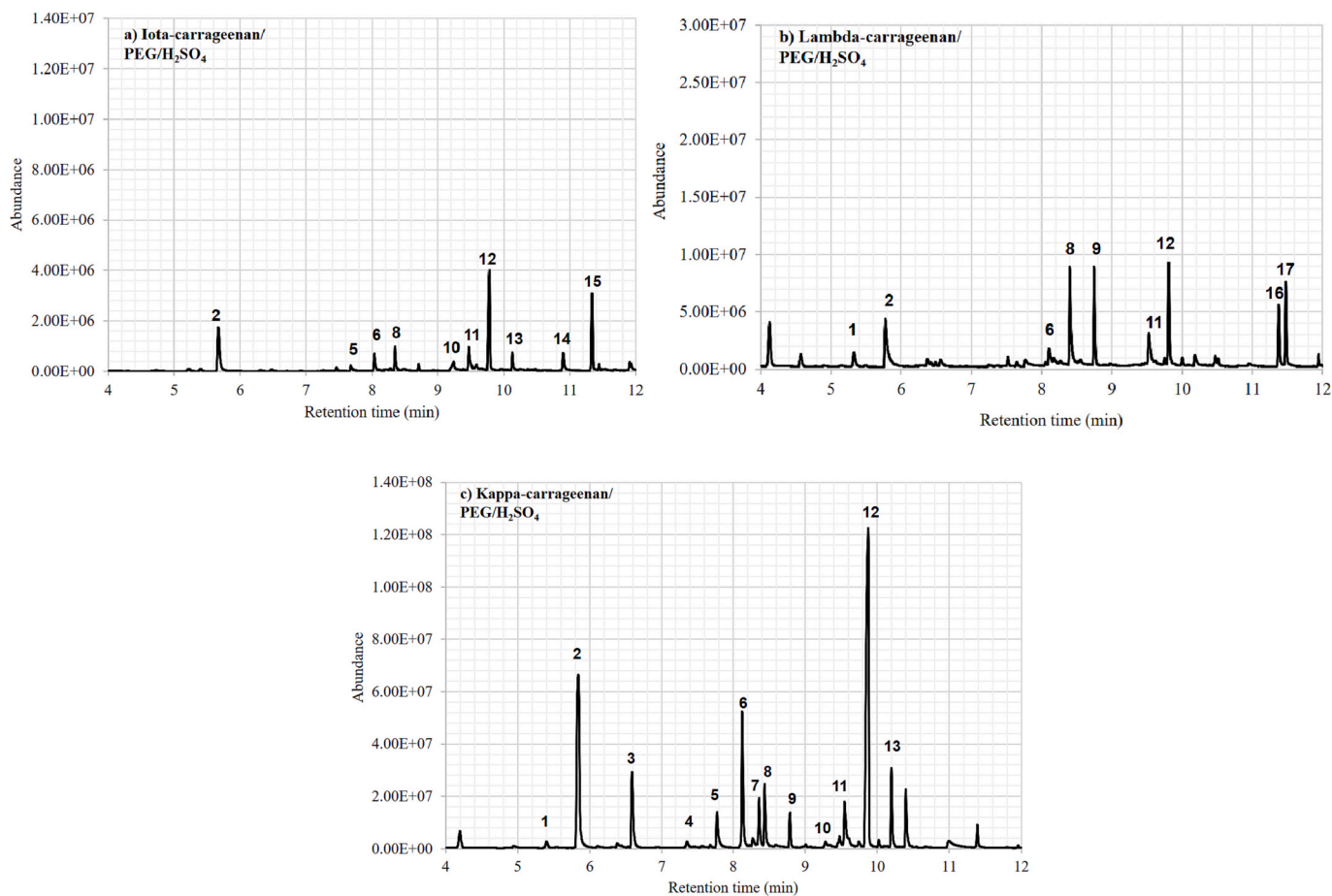Fig. 5 shows the average yields (mg/g_{carr}) of LGO and furfural from

Fig. 4. Gas chromatogram of volatile compounds evolved from acid-catalyzed pyrolysis of iota-, lambda-, and kappa-carrageenan in PEG. Peak 1 is solvent-derived (butyl acetate) and peak 9, 16, and 17 are crown ethers.

the neat and acid-catalyzed pyrolysis from each of the three carrageenans. The primary distillate collected from the pyrolysis contained varying amounts of water, and so for meaningful analysis the masses of distillate were converted to LGO and furfural quantities using the relative response factor and internal standard. The use of H_2SO_4 in the pyrolysis improved the overall yield, as acid may promote the thermal decomposition of carbohydrates and accelerate the pyrolysis reaction (Xu et al., 2022). The yields of LGO and furfural during the uncatalyzed pyrolyses were highest for kappa-carrageenan, followed by iota- then lambda-carrageenan. Catalyzed pyrolyses in PEG gave higher yields for kappa- and iota-carrageenan, followed by lambda-carrageenan. Kappa-carrageenan has on average a single sulfate ester per disaccharide repeating unit and generated the most LGO (17.6–25.0 mg/g_{carr}) and furfural (4.8–7.1 mg/g_{carr}). Iota- and lambda- have the same quantities of total sulfur. However, iota- produced more LGO (9.1–12.3 mg/g_{carr}) and furfural (2.7–3.0 mg/g_{carr}) than lambda-carrageenan (3.1–4.7 mg/g_{carr} and 1.1–1.3 mg/g_{carr} for LGO and furfural, respectively). Iota-carrageenan also contains 4-linked 3,6-anhydro-D-galactopyranose groups, which are not present in lambda-carrageenan. This structure may have caused higher yields of LGO and furfural, particularly during pyrolysis with PEG and H_2SO_4. This motif is also present in kappa-carrageenan, which produced the largest yields of LGO and furfural. These results demonstrate that the sulfate ester group in carrageenan may inhibit the formation of both LGO and furfural, while the 4-linked 3,6-anhydro-α-D-galactopyranose structure may cause higher yields of LGO and furfural during acid-catalyzed pyrolysis in PEG. These findings fit with the proposed mechanism for the formation of LGO from pyranose sugars previoulsy discussed (Rodiahwati et al., 2023). 1,4:3,6-Dianhydroglycopyranose and other 3,6-anhydropyranose derivatives have

been shown to lead to LGO with small energy barriers (Greatrex et al., 2017), and in some instances at sub-ambient temperatures (Griffen et al., 1994).
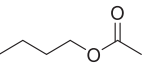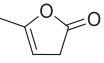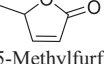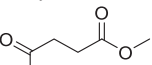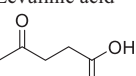
The percentage molar yields of the LGO following acid-catalyzed pyrolysis in PEG are 2.2 mol% (iota-), 1.0 mol% (lambda-) and 3.5 mol% (kappa-). Compared to cellulose pyrolysis unde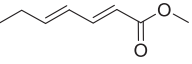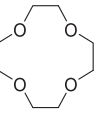r similar conditions (Klepp et al., 2020), the yields from the carrageenans are low. LGO production from the acid-catalyzed pyrolysis of cellulose in PEG reported by Klepp et al. (2020) was 18 mol%, while the highest LGO yield, from kappa-carrageenan was only 3.5 mol%. Molar yields of furfural are also very low: 0.7 mol% (iota-), 0.4 mol% (lambda-) and 1.3 mol% (kappa-). These low yields may be a consequence of the more complicated carrageenan structures, with the presence of galactopyranose in carrageenan compared with glucopyranose in cellulose. This leads to a broader range of pyrolysis products and hence lower selectivities and yields.

4. Conclusion

Preliminary DSC experiments determined that mixing carrageenan with H_2SO_4 and PEG significantly lowers and broadens the temperatures of the decomposition exothermic peaks for all three polysaccharides analysed in this work. Peak temperatures were lowered by between 33 and 60 °C. The total sulfur content in the pure carrageenans correlated well with the DSC peak temperatures of the uncatalyzed polysaccharides. Preparative-scale pyrolysis of the three carrageenans (iota-, lambda- and kappa-) produces LGO and furfural as the major evolved products. Yields are significantly increased when the pyrolyses occur in mixtures of PEG and H_2SO_4. The sulfate ester group in carrageenan may

Table 1

TIC percentages of volatile compounds identified from the acid-catalyzed pyrolysis of iota-, lambda-, and kappa-carrageenan in PEG (Reference: NIST Library). Peak 1 is a solvent derivative and peaks 9, 16, and 17 are crown ethers and were excluded in the calculations. Numbers in brackets are from acid-catalyzed pyrolysis of pure carrageenans (without PEG and H_2SO_4).

| Peak #	Ret Time	Compound	% Area		
			Iota-carr	Lambda-carr	Kappa-carr
1	5.403	Butyl acetate		*From solvent*	
2	5.840	Furfural	12.3(10.8)	26.1(12.0)	32.3 (38.7)
3	6.590	5-Methyl-2(3*H*)-furanone	- (4.1)	- (-)	9.7 (1.0)
4	7.358	2-Acetylfuran	- (-)	- (-)	1.0 (9.8)
5	7.776	5-Methyl-2(5*H*)-furanone	2.2 (6.5)	- (4.1)	4.2 (1.4)
6	8.128	5-Methylfurfural	4.0 (1.8)	5.1 (2.8)	14.4 (4.4)
7	8.362	Isomaltol	- (-)	- (-)	3.4 (8.2)
8	8.440	Methyl levulinate	5.6 (-)	29.3 (-)	4.6 (-)
9	8.789	[1,4,7] Trioxonane		*Crown ethers*	
10	9.253	Levulinic acid	8.5 (2.7)	- (-)	0.5 (-)
11	9.560	Furyl hydroxymethyl ketone	8.5 (12.7)	13 (21.9)	1.4 (8.5)
12	9.852	LGO	18.7 (61.4)	26.5 (59.2)	27.4 (28.0)
13	10.199	Dimethyl hepta-2,4-dienoate	4.1(-)	- (-)	1.1 (-)
14	10.931	Not-identified	12.1 (-)	- (-)	- (-)
15	11.348	Not-identified	24.0 (-)	- (-)	- (-)
16	11.378	Crown ethers			
17	11.481	12-Crown-4		*Crown ethers* *Crown ethers*	
		Total %	100 (100)	100 (100)	100 (100)
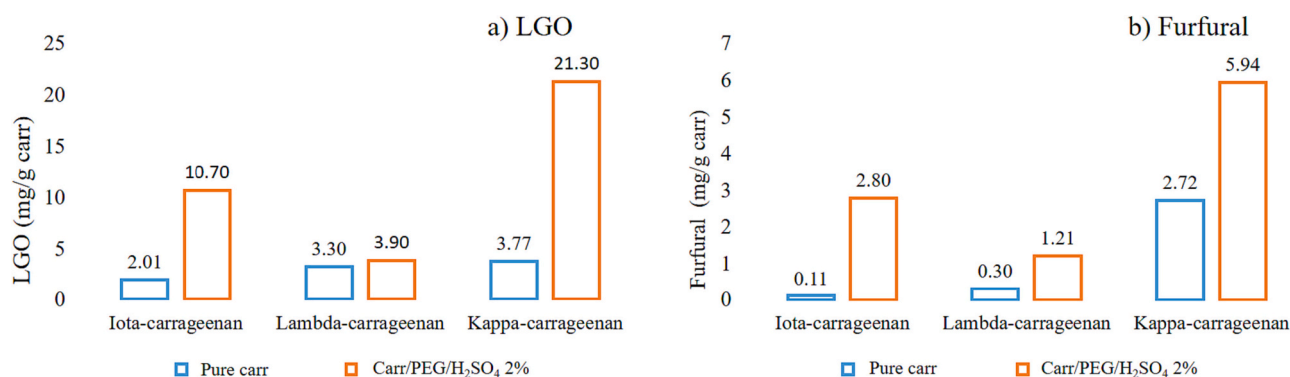
Fig. 5. Average yields of a) LGO and b) furfural in pyrolysis of carrageenan with and without PEG and H_2SO_4.

inhibit the formation of volatile products, while the presense of the 3,6-anhydro-D-galactopyranose structure correlated with higher production of LGO. This work is the first investigation of the fine chemicals produced by the acid-catalyzed pyrolysis of three carrageenans (iota-, lambda- and kappa-). Kappa-carrageenan, with a single sulfate ester group and containing the 3,6-anhydro bridge gave the highest LGO and furfural yields compared to iota- and lambda-carrageenan. Yields of LGO are low compared with the acid-catalyzed pyrolysis of cellulose in PEG. Nevertheless, this study has shown the potential of valorising galactan marine biomass into LGO which is a valuable chiral platform molecule.

CRediT authorship contribution statement

Wawat Rodiahwati: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Trevor C. Brown:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Supervision, Writing – review & editing. **Ben W. Greatrex:** Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biteb.2023.101576.

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