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Paper

Fuel intermediates, agricultural nutrients and pure water from *Kappaphycus alvarezii* seaweed

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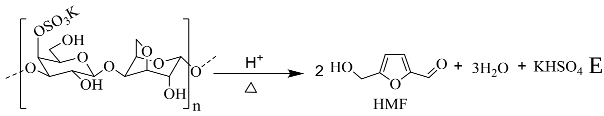
The present work reports a standalone integrated scheme for the production of 5-hydroxymethyl furfural (HMF) and potassium sulphate (K_2SO_4) from granular biomass rich in the sulphated polysaccharide, κ-carrageenan. Fresh *Kappaphycus alvarezii* seaweed was crushed to expel the juice rich in KCl (0.7 m^3/t of fresh seaweed) and granular biomass (0.04 t dry weight/t of fresh seaweed). The latter yielded κ-carrageenan through seawater extraction. HMF was derived from this phycocolloid through reaction with $Mg(HSO_4)_2$ acid catalyst and isolated in pure form. Galactose was a co-product which remained in the aqueous phase. The aqueous phase was recycled up to 10 times by maintaining a constant acid strength, and utilized thereafter for the recovery of K_2SO_4. Selective crystallization of K_2SO_4 was guided by the phase diagram and use was made of a part of the seaweed juice in this process. The spent aqueous phase rich in galactose was subjected to further reaction with HCl obtainable through bipolar electro-dialysis (ED) of seaweed juice. The reaction yielded levulinic acid (LA) and formic acid (FA) in nearly equal proportions. The processing of 1 t of granular biomass was computed to require 30.15 GJ of energy and would yield 0.18 t HMF, 0.056 t LA, 0.020 t FA, 0.27 t K_2SO_4, and 5.77 m^3 pure water. The process energy requirement for the scheme can be met from additional supplies of granule (3.35 t). Combustion/gasification of this biomass would yield additionally 0.74 t glaserite fertilizer and the required amount of H_2SO_4 for $Mg(HSO_4)_2$ preparation.

Introduction

Whereas solar energy, wind energy, nuclear energy, hydroelectric power, and geothermal energy can meet the demand for thermal and electrical energy in part or in full,[1-4] the production of liquid fuels for sustainable mobility will remain critically dependent on biomass, even considering the future scenario of partial replacement of conventional vehicles with electro-vehicles and hybrids. Many types of terrestrial biomass have been used for this purpose, but the potential of fast growing seaweeds remains unexploited.[5-8] Bioethanol and several other liquid fuels can be readily produced from this alternative feedstock as essentially the same chemical processes are involved as in the case of land-based carbohydrate biomass conversion. These conversions typically involve hydrolysis of polysaccharides to simple sugars and further conversion of the sugars into ethanol through fermentation or into other fuels through dehydration, rearrangement/ fragmentation and hydrogenation.[6] Besides circumventing the dilemma of land use competition for food and fuel, their cultivation in the sea can be carried out without inputs of fresh water, fertilizers and pesticides, and the polysaccharides present in many cultivable seaweeds are easier to process for fuel than cellulosic biomass.[9] Countries such as India which have a long coastline can better exploit their geographical advantage and look to the sea for biomass.

The red seaweed, *Kappaphycus alvarezii*, is easy to cultivate, exhibits prolific growth, and sequesters 17-20 t of CO_2/hectare/annum.[10] One hectare of cultivation can generate 300 t of fresh biomass annually from which 210 m^3 (70 % (*v*/*w*)) of juice and 12 t (dry basis) of granule (4 % *w*/*w*) are obtained. The former finds application as leaf spray whereas the latter yields κ-carrageenan, a linear sulphated polysaccharide.[11] Besides its known applications, κ-carrageenan has been utilised for ethanol production .[12-13] The seaweed also accumulates potassium from seawater with K^+/Na^+ selectivity ratio in excess of 350. The K^+ is present as ca. 4 % (*w*/*v*) KCl in the juice and as counter ion in the polysaccharide.

In the course of investigations to improve the ethanol yield from the granular biomass,[13] it was observed that hydroxymethyl furfural (HMF), formic acid (FA) and levulinic acid (LA) were formed as impurities during hydrolysis.[14a] Similar observation was made by Meinita *et al.*, who investigated the inhibitory effect of these compounds on fermentation.[14b] The production of such compounds may be of greater interest than production of ethanol.[6,15-19] Kim *et al.* have shown that a mixture of HMF and LA can be obtained from agar. The process entailed use of ionic liquid and chromium salt besides a solid acid catalyst.[6c] The present work reports the production of HMF from κ-carrageenan using benign $Mg(HSO_4)_2$ as catalyst.[20,21] Whereas Eq. 1 shows an idealised reaction with 100 % carbon utilisation efficiency towards HMF formation, galactose was obtained as co-product in the study and converted separately into LA and FA. Other useful products – most importantly potassium sulphate fertilizer – accrued from the integrated approach.[20] The neutralized aqueous stream after HMF recovery, along with a part of the seaweed juice, were utilised for this purpose. Isolation of K_2SO_4 formed via the reaction of Eq 2 was guided by the phase diagram of reciprocal salt systems.[22] It is proposed that the process energy requirement can be met from seaweed biomass itself.



Eq 1

$$K_2SO_4.MgSO_4.6H_2O + 2KCl \longrightarrow 2\,K_2SO_4 + MgCl_2 \qquad \text{Eq 2}$$

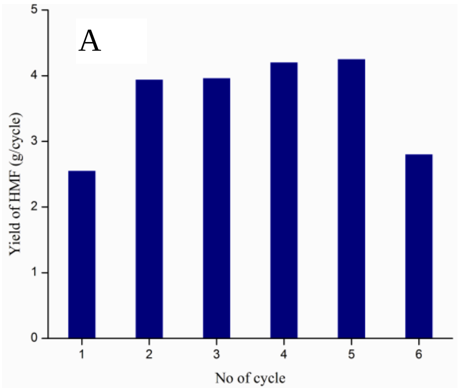
Results and Discussion

The granular mass obtained from *K. alvarezii* comprises cellulose and κ-carrageenan present in similar proportions. The hot aqueous extractive was filtered to separate out the cellulosic matter and thereafter κ-carrageenan was isolated through precipitation with isopropyl alcohol (IPA). The sulphate content was 21.5 % (*w/w*), which matched well with the expected value of 22.64 % (*w/w*) for a structure bearing one sulphate half ester per repeating unit of pristine κ-carrageenan (*MW* = 424). The potassium content was 7.7 % (*w/w*) which indicated that the counter ion for ca. 85 % of the half ester groups of the repeating units was K^+, the remaining being Na^+ primarily. Characteristic bands due to 4-sulphate and 3,6-anhydro galactose were seen in the IR spectrum (Figure S1). Co-production of HMF and K_2SO_4 in integrated manner from the pristine κ-carrageenan via Eqs 1 and 2 was considered an attractive proposition and the methodology was formulated accordingly. The residual mass after recovery of the carrageenan was dried and gave a calorific value of 14.6 MJ/kg with negligible ash formation.

HMF synthesis

Although several methods for HMF synthesis have been listed in a recent review on the subject – including synthesis in ionic liquids and other non-aqueous media[23] – aqueous H_2SO_4 was considered initially in the present scheme as it could be obtained through combustion of the granules. This is discussed below. The H_2SO_4 concentration was varied from 0.1N to 0.9N and the reactions were conducted with 5 % (*w/v*) κ-carrageenan under autoclave condition at 105°C (see SI for details, Figure S2). HMF was recovered through its extraction with ethyl acetate. In comparison to the 100 % carbon utilisation efficiency for the idealised reaction of Eq 1, the best result obtained was 49% of isolated HMF at 0.3N acid concentration (Table 1). Lower concentrations gave less reaction while at higher concentrations HMF was found to degrade to LA (Figure S3). Maintaining acid concentration thereafter at 0.3N, the reaction time was increased to 2 h which raised the yield of HMF to 52.6 % with only marginal drop in selectivity (entry 7, Table 1). Further increase of the time to 3 h was found to be deleterious (entry 8, Table 1), due to the degradation of HMF to LA. Thereafter a study was conducted with 0.3N H_2SO_4 to ascertain recyclability of the acidic aqueous layer after HMF extraction. The HMF yield rose in the second cycle and then remained steady till the fifth cycle. Beyond this, the yield and selectivity dropped markedly (Figure 1A). With the assumption that the decline was due to build up of $KHSO_4$ over the cycles on account of hydrolytic cleavage of the sulphate moiety in the substrate (Eq 1), it was decided to maintain the acid concentration constant over the cycles through neutralization of the excess acid generated. However, since H_2SO_4 would be converted to bisulphate during neutralization, a better option would be to use bisulphate catalyst initially itself. $Mg(HSO_4)_2$ was chosen since it was inexpensive to prepare from H_2SO_4 and $Mg(OH)_2$ and also to facilitate recovery of K_2SO_4 (see K_2SO_4 recovery section). Table 2 provides data on the reaction with the above catalyst. HMF formation was sensitive to catalyst concentration in the range of 0.33-0.63 M. The best result was obtained with 0.48 M catalyst when similar κ-carrageenan concentration and reaction conditions were adopted. Higher catalyst concentration led to partial degradation of HMF and/or competing reactions leading to formation of LA. This concentration was therefore selected for the further studies.

The feasibility of recycling the acidic aqueous layer was studied next, taking 100 g κ-carrageenan (6.1 % (*w/w*) moisture content) in 10 lots of 10 g each. After each cycle, the aqueous layer was extracted with ethyl acetate and the HMF yield and selectivity estimated by HPLC (Figures S4-S5). The total yield of isolate was 36.05 g, with purity of 92 % based on HPLC assay. The cycle-wise data are plotted in Figure 1B. It can be seen that, as observed with H_2SO_4 (Figure 1A), there was a sharp rise in the yield of HMF over the first two cycles. Thereafter, the yield was similar with a standard deviation of ± 0.16 g for cycles 3-10. The residual HMF in the aqueous phase after each cycle was also analysed directly by HPLC and its amount after cycles 1 and 2 were estimated to be 0.51g and 0.24 g, respectively (Figure S6). For cycles 3-10 the values ranged from 0.19-0.28 g. Thus whereas in the first cycle, 15.4 % of total HMF remained in the aqueous phase, there was no such loss in the second cycle as HMF concentration in aqueous phase was already at the saturation limit; if anything, its solubility was slightly reduced due to salting out effect which may have additionally led to some of the HMF from cycle 1 being accounted for in cycle 2. Thus the substantial difference in the HMF yields between first and second cycles could be rationalised.



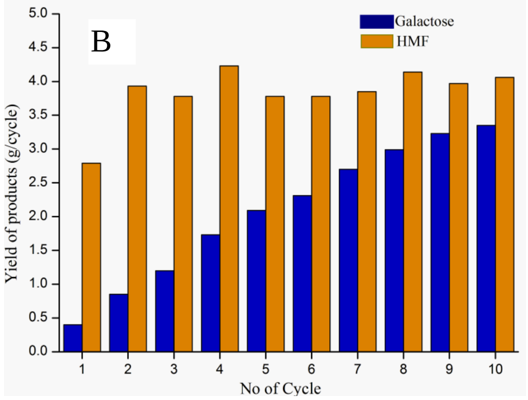


Fig. 1 Bar diagram of (A) HMF content in ethyl acetate fraction with 0.3 N H_2SO_4 as catalyst and reuse of the acidic aqueous phase and (B) HMF and galactose yield for 10 cycles with reuse of acidic aqueous phase (10g κ-carrageenan was added in each cycle, catalyst was 200 mL 0.48 M $Mg(HSO_4)_2$ and reaction condition was 105ºC for 1h in autoclave (standard deviation : ± 0.16 g for cycles 3-10).

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Taking the total HMF formation (34.47 g on 100 % purity basis) into consideration, the carbon conversion efficiency worked out to 61.8 %. An attempt was made thereafter to account for the remaining carbon in κ-carrageenan. Galactose was found to be a co-product of the reaction (Figure S7), and it can be seen from Figure 1B that its concentration grew almost linearly over the 10 cycles. The total amount of galactose formed was estimated to be 20.84 g corresponding to a carbon utilisation efficiency of 26.1 % on κ-carrageenan basis. Thus the total carbon utilisation towards formation of HMF and galactose was 88.0 %. A second experiment conducted with 100 g κ-carrageenan over 10 cycles, and a third with 120 g κ-carrageenan over 6 cycles, gave similar results. Under the experimental conditions adopted for HMF production from κ-carrageenan, galactose gave virtually no HMF.[24]This accounted for its steady build up over the 10 cycles as shown in Figure 1B.

Table 1 Data on yield and selectivity of HMF formation from κ-carrageenan in autoclave as a function of H_2SO_4 concentration

Entry	Amount of feed (κ-carrageenan) taken g/(mmol)	Catalyst H_2SO_4 (N)	Solvent H_2O (mL)	Time (h)	HMF (% of carbon utilisation)	Selectivity of HMF in organic part (%)[a]
1	1/(2.36)	0.1	20	1	NR	NR
2	1/(2.36)	0.2	20	1	<20	low
3	1/(2.36)	0.3	20	1	49	100
4	1/(2.36)	0.5	20	1	41	68
5	1/(2.36)	0.7	20	1	34	54
6	1/(2.36)	0.9	20	1	30	50
7	1/(2.36)	0.3	20	2	52.6	98
8	1/(2.36)	0.3	20	3	50.8	91

[a] GC selectivity

Table 2 Data on yield and selectivity of HMF formation from κ-carrageenan in autoclave as a function of $Mg(HSO_4)_2$ concentration

Entry	Amount of feed (κ-carrageenan) taken g/(mmol)	Solvent H_2O (mL)	Catalyst $Mg(HSO_4)_2$ (M)	Time (h)	HMF (% of carbon utilisation)	Selectivity of HMF in organic part (%)[a]
1	2.5/(5.9)	50	0.33	1	NR	NR
2	2.5/(5.9)	50	0.38	1	25.5	99
3	2.5/(5.9)	50	0.43	1	32.8	99
4	2.5/(5.9)	50	0.48	1	42.3	99
5	5/(11.8)	100	0.48	1	43	99
6	5/(11.8)	100	0.53	1	31	80
7	5/(11.8)	100	0.63	1	27	78

[a] GC selectivity

A mechanism is proposed in Figure 2 to rationalise the co-formation of HMF and galactose from κ-carrageenan in the relative proportions indicated. As can be seen from the figure, one part of the repeating unit possesses a 1,3 linked α-D-galactopyranose unit sulphated at the C-4-position whereas the other part comprises a 1,4 linked strained β-D-3,6-anhydro galactose unit. On acid induced cleavage of the glycosidic linkages,[6c] these two units are assumed to form the intermediates 1 and 2, respectively. 2 may rearrange to 4 upon addition of H_2O. Relief of ring strain would provide the driving force for the facile conversion of 4 into HMF. 1 can either yield galactose and $KHSO_4$ by pathway (i) or it can give the carbocation intermediate 3 which too can generate HMF. The formation of HMF via the two pathways would explain the greater than 50 % carbon utilisation efficiency from κ-carrageenan. The criticality of optimizing the acid strength was on account of the competition among the different pathways and the hydration/dehydration sequences involved which are strongly acid sensitive.

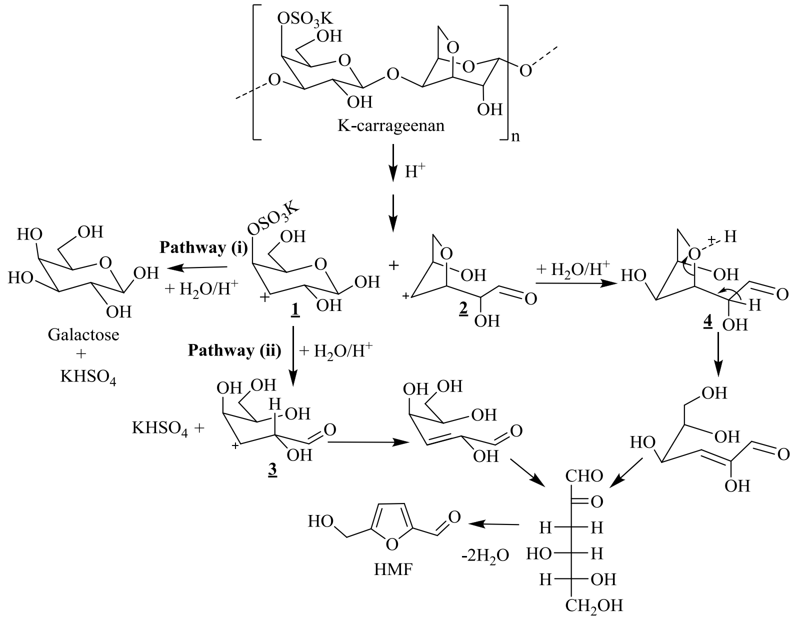

Fig 2 Proposed mechanism of HMF formation from κ-carrageenan

Utilisation of aqueous layer

A. K_2SO_4 recovery

The neutralized spent aqueous phase (0.25 L) obtained from the experiment with 120 g κ-carrageenan was found to contain 6.9 g K^+, 10.6 g Mg^{2+} and 50.6 g SO_4^{2-} as the main inorganic constituents. SO_4^{2-} was derived both from the substrate and catalyst employed, and its total amount was in good agreement with the expected value of 53.2 g. When expressed in terms of the concentrations of K_2SO_4 and $MgSO_4$, the values were computed to be 8.42 and 42.05 mol/1000 mol H_2O, respectively (Table S1). The above composition fell within the schoenite (K_2SO_4. $MgSO_4.6H_2O$) field in the Lowenherz phase diagram (Figure 3, point 1). To effect the conversion of Eq 2, seaweed juice was added into the solution to shift the equilibrium of the composition to K_2SO_4 field (point 2). Progressive forced evaporation gave 1.5 L of distilled water in total. The water, after treatment through carbon filter, had a pH of 7.1 and was free of any odour. The value of total dissolved solids (TDS) was 80 mg.L^{-1}, the TOC was 17.53 mg.L^{-1} (the corresponding value for potable water consumed routinely was 32.79 mg.L^{-1}) and the heavy metal concentration was less than 0.02 ppm. Evaporation of the water shifted the equilibrium of the composition progressively from point 2 to point 7 in Figure 3. 66.8 g K_2SO_4 (73 % yield on sulphate basis) (Table S1) was obtained and its powder XRD matched well with the standard (Figure S8). Further evaporation gave a composition which fell in the KCl field (Figure 3, point 8). The observed trends suggest that the effect of dissolved sugars was not pronounced. The mother liquor after recovery of K_2SO_4 contained the by-product galactose obtained during HMF synthesis and resembled molasses in appearance.

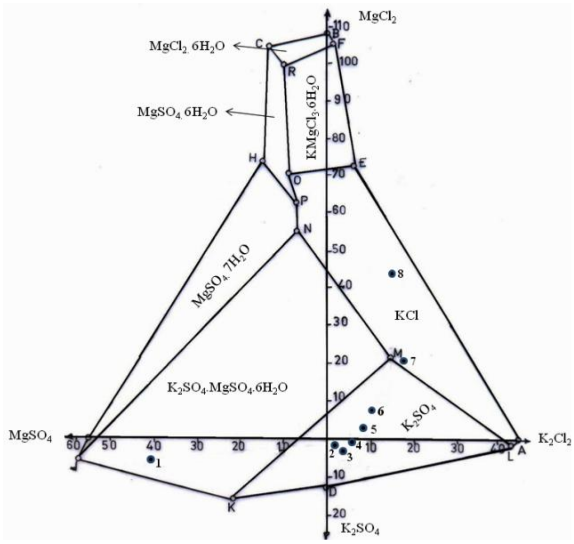

Fig 3 Experimental data points of composition of spent aqueous phase after HMF recovery (filled circle 1), after addition of seaweed juice containing KCl (filled circle 2) and subsequent evaporation in stages (filled circles 3-8) superimposed on the Lowenherz representation of the phase diagram at 25°C for reciprocal salt pairs. The orthogonal axes indicate concentrations of the salts in mol/1000 mol H_2O.[22]

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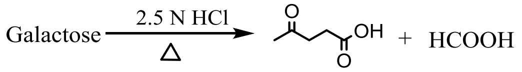
B. Levulinic acid synthesis from by-product galactose

The synthesis of LA from cellulose, starch, other polysaccharides and sugars is well known. 63.1 % yield of LA was reported from cellulose employing a polymeric ionic liquid.[25a] Reactions are also reported with sucrose, starch, cellulose and chitosan, with yields in the range of 32-46 % employing HCl catalyst.[25b-f] LA has also been synthesized from galactose, derived from *Gelidium amansii*. A yield of 41.4% was obtained at 160°C using 5 % H_2SO_4 catalyst.[25g] Synthesis of LA from galactose obtained as by-product during HMF synthesis from κ-carrageenan would be of interest. HCl, which can be obtained from seaweed juice through bipolar electrodialysis (bipolar ED) (Figure S9), was selected as the catalyst of choice. An experiment was undertaken with the neutralized aqueous layer from the experiment of Figure 1(B). The solution was desulphated and reacted under autoclave condition at 105°C for 1h using 2.5 M HCl as catalyst. 11.06 g LA and 4.02 g FA were obtained in 82.4 % and 76.2 % yield, respectively, considering the reaction of Eq. 3 (Figure S10). Both products are valuable commodity chemicals. The two together can also yield γ–valerolactone, a molecule with diverse applications, including as fuel additive.[17] Production of LA from the galactose present in the molasses after recovery of K_2SO_4 was also studied. The isolated yield of LA in ethyl acetate extract was 64.7 %. The aqueous fraction after recovery of LA may be treated to recover $Mg(OH)_2$ required in $Mg(HSO_4)_2$ synthesis, and the filtrate utilised for fortification of the juice.[26]



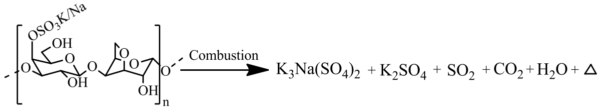
Eq 3

Energy computation

The energy requirement for implementation of the above processes was computed. Individual data for the different steps are provided in Table 3. It can be seen that, to obtain HMF, K_2SO_4, LA, formic acid and pure water in integrated manner, 30.15 GJ of energy would be required per ton of granules processed. Of this amount, 2.67 GJ can be met from the solid residue obtained during extraction of κ-carrageenan. The remaining energy can be sourced from unprocessed granule, with additional gains as discussed below.

Combustion of granules

The use of unprocessed granule as fuel is proposed to meet the process energy requirement (Figure 4). The granules had a calorific value of 2825 kcal/kg (11.87 MJ/kg) and 3.35 t would be needed to meet the thermal energy requirement, assuming 65 % thermal efficiency. Ignition of the granule provided useful products additionally. Ash was obtained in 22 % (*w/w*) yield and weight percentages of K, Na and SO_4^{2-} were 37.3 %, 5.9 % and 55.6 %, respectively, while the chloride amount was negligible. Its powder XRD revealed a mixed composition of $K_3Na(SO_4)_2$ (glaserite) and K_2SO_4, in 9:1 ratio (*w/w*) (Figure 5). The ash may, therefore, find direct application as K+S fertilizer. In a separate experiment, the flue gas released from combustion of washed granule at 800°C in a tubular furnace under continuous air flow was bubbled through 800 mL distilled water. The pH of the water reduced to 2.6 and titration gave an acid strength of 0.0067 N.



Eq 4

Fig 4 Combustion of granules in a solid fuel fired boiler

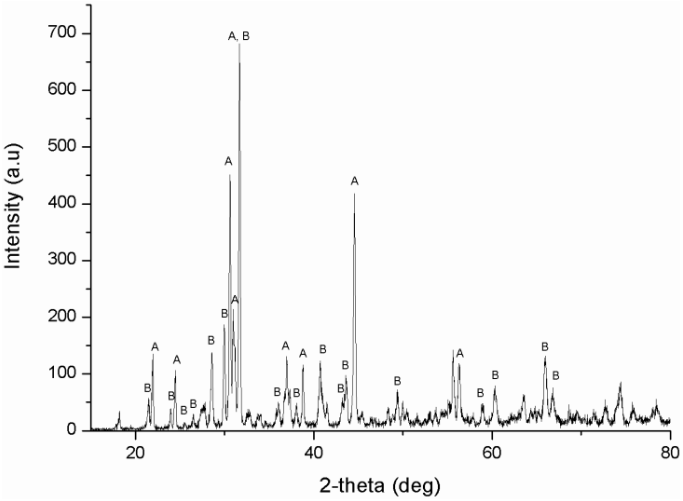


Fig 5 Powder XRD of potash rich fertilizer (two principal phases were glaserite $[K_3Na(SO_4)_2]$ (A) and K_2SO_4 (B)) in the form of ash obtained after combustion of dry granules at 550°C. Search match analysis was performed with high score plus software using ICDD-JCPDF data base.

CO_3^{2-}, SO_4^{2-} and Cl^- were not detected in any substantial amount whereas SO_4^{2-} was detected by $BaCl_2$ test after addition of H_2O_2. Quantitative measurements gave 0.0256 g SO_4^{2-}/g of granule. For the experiment of Figure 1B with 100 g κ-carrageenan, the requirement of H_2SO_4 was 18.62 g. The granule amount which would be needed for process energy is 670 g, yielding 17.52 g H_2SO_4 through combustion, i.e., the requirement and production of H_2SO_4 are closely matched.[27] Small amount of electrical energy required for bipolar ED too can be met from the granule through controlled gasification. The standalone integrated scheme for total utilization of fresh *K. alvarezii* is shown in Figure 6.

Table 3 Computation of input energy for processing of 1 t of *K. alvarezii* granule into useful products. Calculations were based on the laboratory scale data.

Sr. no	Parameter	Energy requirement (GJ)
1.	Autoclaving of granules followed by separation to obtain ~3.8 % solution of pristine κ-carrageenan and solid residue.	6.26
2.	Gel pressing to 8 % κ-carrageenan concentration	0.58
3.	Distillation of IPA used for κ-carrageenan precipitation	7.23
4.	HMF synthesis from κ-carrageenan	3.13
5.	Distillation of EtOAc used for HMF extraction	2.63
6.	Multiple effect distillation for K_2SO_4 production and water recovery	7.8
7.	LA synthesis from molasses (i) Energy requirement for autoclaving (ii)Energy requirement for distillation of EtOAC (iii) HCl and KOH production from KCl rich seaweed juice by bipolar ED	 0.28 0.45 1.79
8.	Total energy requirement for 1-7	30.15

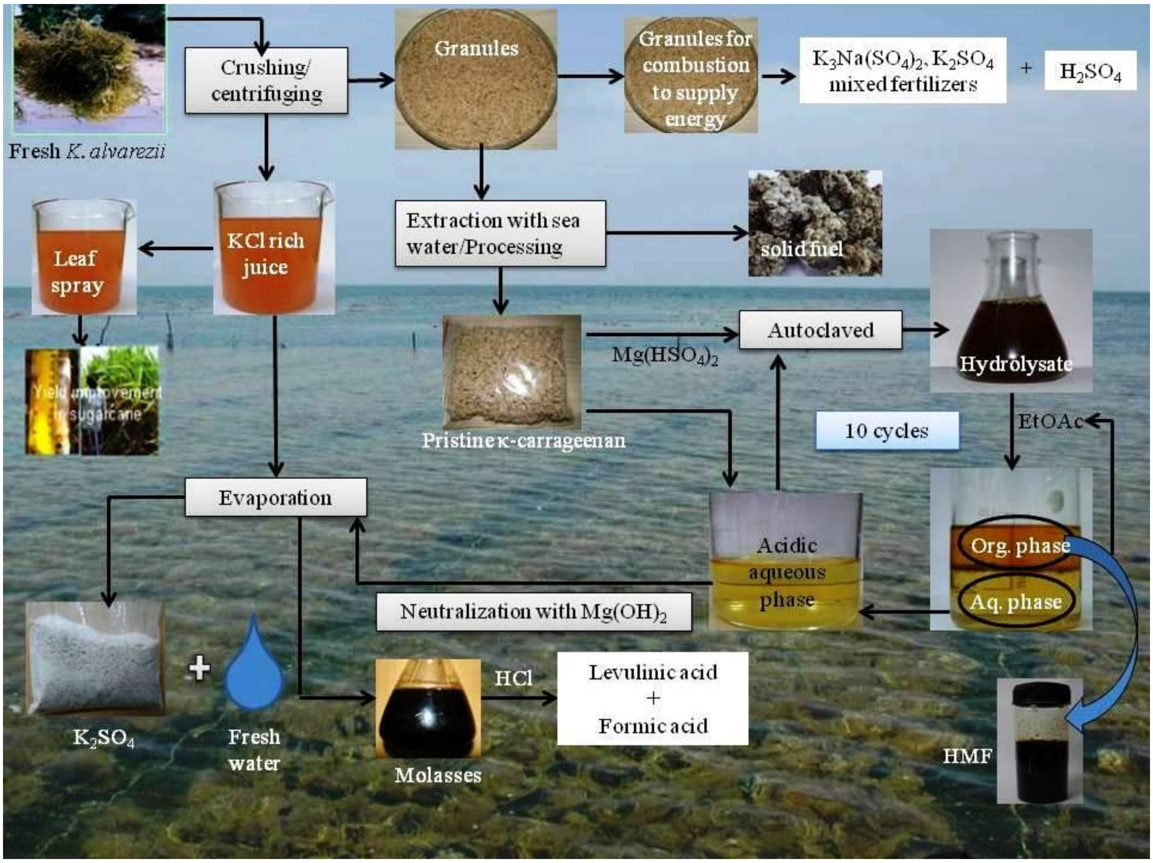


Fig 6 Integrated scheme for total utilisation of fresh *Kappaphycus alvarezii* red seaweed

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Conclusion

The present study set out to demonstrate the production of HMF and K_2SO_4 fertilizer from the fast growing cultivable seaweed, *K. alvarezii*. The overarching principles adopted while formulating the strategy may be stated as follows:

(1) Realise the full potential of the biomass
(2) Identify and exploit synergies
(3) Avoid chemical inputs which do not form part of the product portfolio
(4) Generate catalysts as part of the integrated process
(5) Make the operation standalone.

As would be evident from Figure 6, these objectives were achieved and useful synergies identified while developing the integrated scheme. $Mg(HSO_4)_2$ was found to be a mild and efficient catalyst for HMF synthesis. It also had a role to play in K_2SO_4 recovery from the aqueous stream. Fresh water of desired quality was a co-product, a portion of which can be recycled in the process. The surplus would be a precious commodity in water-stressed coastal locations. The aqueous stream additionally gave LA and FA using HCl as the catalyst. HCl can be generated from seaweed juice through bipolar ED. The combined carbon utilisation efficiency was 83.0 % for the formation of HMF, LA and FA from κ-carrageenan. The spent aqueous stream may be utilised to fortify the seaweed juice having utility as leaf spray. Controlled combustion of 3.35 t granule per t of granule processed can provide the thermal energy to drive the integrated process, besides also yielding H_2SO_4 and a second potash fertilizer of commercial importance. The former would regenerate $Mg(HSO_4)_2$ through reaction with recycled $Mg(OH)_2$. Considering overall usage of granule to be 4.35 t, the product portfolio shown in Table 4 would be obtained. Given that it is inexpensive to raise the biomass, external inputs of energy and chemicals are minimal, and considering the commercial value of the products derived, the process should be economically viable and merits scale up. To process 1 t of granule per day for 0.18 t HMF and co-products (Table 4) in a bio-refinery, the annual requirement of granule would be ca. 1590 t, inclusive of the granule amount for process energy. This amount is obtainable from cultivation over 125-150 hectare in coastal waters. The small requirement of electrical energy to drive the bipolar ED process too can be met from the granule through gasification. The process would thus be self-sustainable. If the challenges of cultivation on large scale can be dealt with successfully, the scheme proposed offers considerable opportunity to source the products listed in Table 4 with negligible carbon footprint.

Table 4 Details of products and their corresponding amounts obtainable from processing of 1 t of *K. alvarezii* granule using 3.35 t additional granule as energy source.

Product	Amount
5-hydroxy methyl furfural	0.18 t
Levulinic acid	0.056 t
Formic acid	0.020
Potassium suphate	0.27 t
Glaserite	0.74 t
Leaf spray	68.93 m^3
Fresh water	5.77 m^3

Experimental Section

General consideration

Reference samples of HMF and LA were purchased from TCI (Tokyo Chemical Industry Co., LTD), Tokyo, Japan while 98 % H_2SO_4, 12 N HCl and $Mg(OH)_2$ were purchased from S.D Fine Chemicals, Mumbai, India. All chemicals were of analytical grade and were used as received without further purification. Reagent grade EtOAc and IPA were used in the process whereas HPLC grade solvents were used for HPLC and GC-MS analysis.

Analytical Methods

Calorific value was determined by digital Bomb calorimeter (Toshibha India). FT-IR spectra of carrageenan were recorded on a Perkin-Elmer Spectrum GX (FT-IR System, USA) instrument. HMF was characterized by GC-MS and HPLC. GC-MS spectra were recorded on Shimadzu GC-MS QP 2010. HMF, galactose, LA and formic acid were quantified by HPLC (Waters Separation Module 2695, USA) assay. Total sugar concentration present in the hydrolysate was estimated spectrophotometrically by phenol-sulphuric acid method. Sulphate was estimated gravimetrically; Cl^- was estimated using titration method; sodium and potassium were estimated by flame photometry. Powder x-ray diffraction (XRD) measurements were performed on X`pert MPD power X-ray diffractometer using CuKα radiation operating at 40 KV and 30 mA. Data were collected in the range of 2 to 80º 2θ with a step size of 0.05º2θ/sec. Search match analysis was performed with high score plus software using ICDD-JCPDF data base. Total organic carbon content was measured on an Elementar, Liqui TOC machine.

Extraction of κ-carrageenan from granules

250 g of *K. alvarezii* granules (ca. 8 % moisture content) obtained from the fresh seaweed after expelling the seaweed juice mechanically was taken in 5L seawater and autoclaved at 105ºC and 30 kPa pressure for 60 minutes. The contents were hot centrifuged to obtain 70 g of residue (30.4 % yield on dry granule basis) having calorific value of 3473 Kcal/kg. 120 g of pristine κ-carrageenan having ~8 % moisture content (48.02 % yield *w/w*) was obtained from the hot aqueous extract through precipitation with IPA (extract : IPA = 1:2 *v/v*). The IPA was distilled from the filtrate and recycled. The moisture content of κ-carrageenan varied in the range 6-8 % (*w/w*).

HMF synthesis from κ-carrageenan

(A) 10 g of κ-carrageenan was taken in 200 mL of 0.48 M $Mg(HSO_4)_2$ (optimized condition) and autoclaved at 105ºC for 1 h. The product mixture was extracted with ethyl acetate. $KHSO_4$ (3.21 g; 23.6 mmol) released during hydrolysis of κ-carrageenan from the previous batch was neutralized with $Mg(OH)_2$ (0.68 g, 11.8 mmol) and 10 g of κ-carrageenan was once again added into the aqueous phase and the procedure repeated utilising recycled ethyl acetate for extraction. After 10 cycles, 36.05 g of HMF was isolated having 92 % purity by HPLC assay. The concentrations of residual HMF and galactose in aqueous stream were also estimated by HPLC without extraction from the aqueous solution. The experiment was conducted in duplicate and the results were comparable.

(B) The experiment at (A) above was repeated with 20 g of κ-carrageenan taken in 300 mL of 0.48 M $Mg(HSO_4)_2$. 6 cycles were carried out at the end of which 42.5 g of HMF was isolated. The aqueous phase measuring 250 mL was neutralized with $Mg(OH)_2$ and the total sugar in it was estimated to be 33.6 g with 80 % galactose. The inorganic constituents in the aqueous phase

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after neutralization were as follows: K^+, 6.9 g; Mg^{2+}, 10.2 g and SO_4^{2-} 50.6 g,

K_2SO_4 recovery from neutralized aqueous stream after extraction of HMF and seaweed juice with simultaneous production of pure water

Recovery of K_2SO_4 was based on the phase diagram of reciprocal salts of quaternary system (Figure 3). The concentrations of K_2SO_4 and $MgSO_4$ in the neutralized aqueous phase from (B) above were computed to be 8.42 and 42.05 mol per 1000mol of H_2O. Into this solution 1.8 L of seaweed juice containing 4.14 % (*w/v*) KCl was added and the contents subjected to progressive evaporation in a rotavap to recover K_2SO_4 in pure form.

Levulinic acid synthesis from galactose co-produced during HMF synthesis

The aqueous stream from HMF synthesis was neutralized and desulphated using $CaCl_2$. 160 mL filtrate containing 20.84 g of galactose was taken and acidified with concentrated HCl to an acid strength of 2.5 M HCl and then reacted in an autoclave under similar conditions adopted for HMF synthesis. 11.06 g of levulinic acid and 4.06 g of formic acid was found to be present (HPLC assay) in the aqueous layer.

In an another experiment the sugar rich molasses after K_2SO_4 recovery (33.6 g, 50 mL) was diluted with 50 mL 5 N HCl and the mixture was autoclaved at 105 °C for 1.5 h followed by extraction with ethyl acetate (4x100 mL). The 1st fraction was discarded and the remaining three fractions were combined. 11.2 g of levulinic acid was obtained in the organic layer.

Combustion of granules for H_2SO_4 production

10 g of dry granule after washing was taken in alumina porcelain and was combusted at 800°C in tubular furnace for 3 h under continuous air flow. The flue gas generated during combustion was bubbled through 800 mL distilled water. The pH of the resultant solution was 2.6 and the acid strength was found to be 0.0067 N through titration. CO_3^{2-}, SO_4^{2-} and Cl^- were not detected in any substantial amount. After treatment of the solution with H_2O_2 (20 % *v/v* of 30 % vol O_2) followed by stirring at room temperature for 30 min, SO_4^{2-} was detected by $BaCl_2$ test. The total amount of SO_4^{2-} obtained was 0.256 g.

Bipolar ED of seaweed juice for generation of HCl and KOH

Bipolar ED was conducted in a homemade ED stack assembled with 5 cell triplets consisting of monopolar interpolymer cation- and anion-exchange membranes and bipolar membrane. The effective surface area of a single membrane was 80 cm^2. The experiments were conducted with 700 mL of seaweed juice containing 4.1 % *w/v* (0.55 M) KCl. The juice was circulated continuously in the electrodialyser between bipolar membrane and cation-exchange membrane (forming alkali stream) and between anion-exchange membrane and bipolar membrane (forming acid stream). A DC electrical potential (40 V) was applied between the two electrodes by an AC-DC rectifier having variable current capacity. Samples of acid and alkali streams were collected at regular intervals and analysed by acid-base titration. After 4.5 h the experiment was terminated. 440 mL of 0.42 M HCl and 390 mL of 0.44 M KOH was obtained.

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