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THE PROSPECTS OF SENSIBLE SOURCES AS HIGH POWER FUEL AND HIGH FIBER PROTEIN

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The sensible sources (namely; corn, wheat, barley, oat and rye) and molasses (procured from the local market of Rawalpindi), following enzymatic hydrolysis were subjected to fermentation to produce high fiber protein (HFP) and liquid protein as a by-product. The former can be used for human consumption and the later was considered fit for animal feed. Carbon dioxide gas produced during fermentation can be used as gas in beverages or converted into dry ice. Malt husk (spent grain) left behind as a result of waste has utilization for poultry and dairy farm. Ethanol produced was converted into high power alcohol and a comparison of its characteristics with those of natural fuels was made. The high power alcohol was transformed into high power fuel (gellified material) by the interaction with potassium salts of the isopropylidene derivatives of carbohydrates. The potassium salt of the isopropylidene derivative of carbohydrate was prepared in two stages: first, derivative of carbohydrates was synthesized by the interaction of carbohydrates with acetone; the derivative so produced was further treated with chlorosulphonic acid in the presence of potassium carbonate, to produce potassium salt of the derivative of carbohydrates. The fermentation mash may be consumed as a non-alcoholic drink after addition of flavor.

Keywords: Sensible sources, Fermentation, Isopropylidene derivative, Gellified material, IR analysis, Thermal study

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1. Introduction

The need for cleaner living and driving has gained lot of attention in the past few decades. The rate of consumption of fossil fuel and its pollution have made it even more glaring issue. Now the sustainability is being sought whatever is planned or done in the fields of housing and transportation. The 1992 Earth Summit of the United Nations exhorted “the need for a development process that does not jeopardize future generations”. The energy sector will have to explore such avenues that ensure the future requirements of not only fuel but also environment-friendly fuel. The initial steps appear to have been taken in 2000 as energy-efficient-windows and solar roof panels, developed by Colorado’s Rock Mountain Institute, decorated the house for the Olympic Games in Sydney, Australia.

Furthermore, electric cars can be seen plying on US and European highways, however, these lack infrastructures for future support and for long-distance traveling, these demand an affordable and readily available system for plugging into. On the other hand, hybrids use both electric motors and gasoline engines. Therefore, search for low-cost and environment-friendly fuel will continue to flourish in the years to come for sustainable development [1].

The petroleum crisis during the 1970s directed efforts at greater reliance on naturally-renewable resources and created an unusually active-interest in fermentation alcohol, as it was considered not only an attractive alternative to fossil fuels but also a potential feedstock for chemical industry.

During the first half of twentieth century, industrial alcohol was produced on a large scale by fermentation. In nineteenth century, however, alcohol produced by different raw materials, was frequently employed, in some countries, for burning purposes only [2]. In this context, UNIDO (United Nations Industrial Development Organization) organized the first international workshop in

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Vienna, Austria on 26-30 March, 1919 on fermentation alcohol to promote its use as fuel and chemical feedstock in developing countries. The use of alcohol for internal combustion engine was promoted as far back as 1894 by Hartman in Leipzig and even Henry Ford I gave much thought to it as an alternative of fossil fuel in the 1930s. This resulted in the Dearborn Conference on what is now called "gasohol" and the establishment of a major fuel (alcohol) plant in Kansas around 1936 (during the 1930s and 1940s). Several developed countries used alcohol-blends and unblended alcohol in many vehicles [3]. Brazil became the leader in 1925, an alcohol-powered Model A Ford was demonstrated but the huge Brazilian Government program (proalcohol) was established as late as 1975 and US Government initiated a substantial program in 1978. About forty countries (including developed as well as developing countries like Pakistan) are in the process of drawing up power alcohol (99% pure ethyl alcohol) [4-6] programs. During 1980s, Pakistan had to base its strategy on molasses as a source of making alcohol [4, 7].

The present research work comprises the fermentation of sensible sources (a term that has been used by Fibertein Corp. Harlan St. Wheat Ridge, Colorado. USA) and molasses, by far the most important raw material for the manufacture of power alcohol as gellified fuel (HPF), and the recovery of other useful by-products such as carbon dioxide (for dry ice, carbonated beverages, etc.), malt husks (for dairy and poultry farms), proteins both solid and liquid (for bakery products and cattle feed) and non-alcoholic soft drinks (for human consumption).

2. Experimental

2.1. Materials

All the chemicals employed in this work were of reagent grade purity. The agricultural materials were procured from local markets of Rawalpindi. All the solutions were prepared in de-ionized water. The derivatives of carbohydrates and their salts were prepared according to known methods.

2.2. General Techniques

The IR spectra were recorded on Hitachi Infrared Spectrometer, Model 270-50 in the range 4000-400 cm^{-1} while TG, DTA and DSC studies were carried out on NETZSCH Simultaneous Thermal Analyzer STA 429 with a temperature programmed furnace. The measurement was carried out with sample size of 30-60 mg. This was heated over the temperature range from ambient to 500^oC in an air atmosphere using kaolin as reference material. The heating rate was 10^oC min^{-1}. The estimation of micro- and macronutrients was performed on Atomic Absorption Spectrophotometer (Hitachi Zeeman Model Z-8000). Carbon, hydrogen and nitrogen were estimated by CHN Perkin Elmer Elemental Analyzer Model 240B. The melting point of all the compounds was measured by Gallenkamp, England.

2.3. Purification of Reagents

2.3.1 Acetone

In acetone (1000 mL), successive quantities of potassium permanganate were added until the violet color persisted. The solution was refluxed for four hrs. After the addition of anhydrous potassium carbonate (100g), the solution was filtered and distilled. Dry acetone obtained in this way was 99.95% pure with refractive index of 1.3554.

2.3.2 Ethanol

In final fermented solution (1L), distilled water (1L) was added followed by distillation of the solution exactly up to volume of 1L gave ethanol content of 4.8% (v/v). Subsequent fractional distillation increased the purity of ethanol to 95%. After pouring the contents (500mL; 95% ethanol) into 1L round bottom flask and adding calcium oxide (125g; 2.23 mol), the mixture was refluxed gently for six hours and kept as such overnight. Further subjection of this mixture to distillation rendered ethanol to a purity of 99.5% (the first 20 mL of distillate were discarded) having a refractive index of 1.3499. In ethanol (50 mL, 99.5%), magnesium turnings (3g) were added. This step was followed by the addition of iodine (0.4g). The mixture was warmed until the iodine disappeared and the heating continued till all the magnesium was converted into ethanolate. After the addition of 450 mL of absolute ethanol (99.5%), the mixture was refluxed for one hr. Distillation of the mixture further increased the purity of ethanol to 99.95% with a refractive index of 1.3596 [8].

2.4. *Composition of Sensible Sources*

The compositions of sensible sources before and after fermentation were determined by the standard methods described in the literature [9-12].

2.4.1 *Moisture (% dry matter)*

Sample (2g) was placed in a crucible with lid and heated in an oven at 105°C for 12 hours. The contents were cooled in a desiccator and weighed. The percentage of moisture was thus calculated gravimetrically.

2.4.2 *Crude protein*

Sample (2g) was transferred to Kjeldhal flask. After the addition of catalyst (5g) [$CuSO_4.5H_2O$, K_2SO_4 and concentrated H_2SO_4 (30 mL) in the ratio of (1:13:3)], the mixture was digested for 30 minutes. The contents were transferred to a 100-mL volumetric flask. After the addition of 5 mL of NaOH (40% w/w), the contents of the volumetric flask were distilled for 5 minutes and the distillate was collected in a flask containing 5 mL of 2% boric acid. Further distillation for 5 minutes and titration against N/5 H_2SO_4 gave the percentage nitrogen content of the sample. It was multiplied by 6.25 to calculate the protein content.

2.4.3 *Fat (ether extract)*

Moisture-free sample (2g) was placed in dry extraction thimble which was plugged with absorbent cotton wool and placed in an extractor. The extract was evaporated to dryness on water bath for 2 hours. The percentage of fat content was calculated.

2.4.4 *Crude fiber*

To the moisture-free sample (2g), dilute H_2SO_4 was added to digest for 30 minutes. The extracted fiber was neutralized with N/10 NaOH solution and after transferring the content to a beaker, 200 mL of boiling dilute NaOH were added. The contents were again digested for 30 minutes. The contents were neutralized with 10 mL hot dilute H_2SO_4 and then 10 mL of hot water were added. The contents were dried at 135°C for 2 hours, ignited at 600°C in a furnace for 30 minutes, cooled in a desiccator and then weighed.

2.4.5 *Ash*

Dried sample (2g) was placed in a crucible and ignited at 600°C for 4 hours. The contents were cooled as above and weighed.

2.4.6 *Carbohydrates (sugars)*

Powdered sample (2g) was dissolved in distilled water (60 mL) and then hydrochloric acid (5 mL) was added to the solution. The contents were kept at 60°C for 2 hours. The pH of the solution was maintained at 7 by addition of NaOH solution (40%). The volume was made up to 100 mL and transferred to a burette. From burette, the solution was added to the boiling liquid [Fehling's solution (5 mL solution A and 5 mL of solution B)] until the blue color of solution became hardly discernible. Then methylene blue solution (indicator 1%) was added and titration was carried out until the blue color of indicator disappeared. The percentage of sugar content was calculated.

2.4.7 *Carbon dioxide*

5 g of fermentable material [wheat, corn, barley, rye and oat including hop (rice, 40%)] was dissolved in appropriate volume of water and the volume was made up to 50 mL. Three traps were connected with the fermentation flasks (each containing 0.1 N barium hydroxide solution). After completion of fermentation, helium gas was flushed through the apparatus and solution from three traps were taken, mixed and titrated against 0.1 N hydrochloric acid using phenolphthalein as indicator. The difference between the volumes of the base gave the volume of carbon dioxide absorbed according to the following equation:

$$1 \text{ mL } 0.1 \text{ N } Ba(OH)_2 = 1.119 \text{ mL of } CO_2 \text{ at N.T.P.}$$

At the beginning of the experiment, 0.1N $Ba(OH)_2$ was titrated against 0.1N HCl to have the first reading for later calculations. From the volume of CO_2 and known volume of fermentable liquid, the percentage of carbon dioxide was calculated.

2.5. *Estimation of Macronutrients and Micronutrients*

The sensible sources were dried first in an electric oven maintained at 40±1°C for 24 hours for the purpose of weight normalization. After complete removal of moisture, the sample was ground in a grinder until fine powder was obtained. An exactly weighed 1.0g of each sample was transferred to a china dish and 10 mL of 65% nitric acid were added to it. The dish was subsequently placed for about 30 min. in oven maintained at 40±1°C. The digested sample was diluted with distilled water (making up the volume to 50 mL) and transferred to a measuring flask (50 mL). This solution was aspirated directly onto the Atomic Absorption Spectrophotometer for the estimation of trace metal content.

2.6. Fermentation

2.6.1 Sensible sources

The sensible sources namely, barley(A), wheat(B), oats(C), rye(D) and corn (maize, E) having weights 250, 100, 150, 200 and 150g, respectively, were converted into malt by steeping for 12 hours (including shaking after every 4 hours) [13,14] followed by filtration. The filtrates were rejected. Residues were stored for germination for 8 days at 18-25°C (humidity, 40-65%) and were regularly shaken after every 12 hours. The germinated product (green malt) contained roots which were rejected and rest of the product was heated at 66°C for 18 hours to collect malt; A = 140g; moisture 5%, B = 90g; moisture 4.5% C = 130g; moisture 5.2% D = 170g; moisture 5% E = 130g; moisture 5%. The malts were then crushed and mixed with hop (rice powder, 60g). The mixtures were changed into slurries by addition of water [15-16, 40]. The slurries were heated at 45°C with stirring for half an hour. Distilled water (1L) was added and further heating continued for 1 hour at 70°C. The products were recovered as light brown syrups (saccharified mesh) and then cooled to 20-30°C (iodine test indicated the complete conversion of starch into sugar). The saccharified mesh was then filtered. The residues (malt husks; 5g) were analyzed. Yeast starter (swollen yeast, 5g) was added to the filtrates (wort; pH, A = 5.4, B = 5.3, C = 5.3, D = 5.4 and E = 5.5). The mixture's temperature (2-4°C) was then maintained for fermentation [17-21]. The fermentation was completed within 7-8 days. Fermented liquids were filtered. The filtrate (50 mL) and residue (50g) from each source were analyzed after filtration [13-21, 40].

2.6.2 Molasses

Molasses (F, sugar 54%) was diluted with distilled water (1L). The solution was kept at density between 1.06 and 1.07 (contained molasses 195 g; sugar 10.8%). The diluted material (solution) was called mesh. Mesh was adjusted to the optimal temperature (25-30°C) and yeast (5g) was mixed (prepared by cultivation of an appropriate organism such as Saccharomyces cerevesiae). The fermentation process was completed in 52 hours. The resulting solution was mixed with distilled water (1L) and distilled at temperature (100°C) until 1L was distilled. The solution was then analyzed.

2.7. Recovery of the Products

2.7.1 Malt husks

The spent grains (5g) recovered during mesh filtration were dried in an oven by maintaining temperature (65°C) for 6 hours. The dried malt husks were obtained.

2.7.2 Solid protein

Solid protein was recovered from fermented material at two different stages. At stage 1, when wort was boiled and centrifuged, the protein was coagulated. After filtration, it was dried at 35±1°C. The protein was recovered as a solid product. At stage 2, fermented mixture was filtered. The residue was dried at 40±1°C for 4 hours. Solid crude protein was isolated. It was further purified in 70% ethanol. The undissolved fibrous material was filtered. Filtrate was diluted with water and the mixture was cooled to isolate 90% solid protein at 35±1°C.

2.7.3 Liquid protein

After the recovery of the solid protein, the liquid protein, present in the filtrate, was recovered by cooling with subsequent centrifugation.

2.7.4 Carbon dioxide

Carbon dioxide evolved during fermentation (contains traces of ethanol vapors, organic components including aldehydes, esters and acetates in addition to air) was passed through the trap 1 containing distilled water, then through traps 2 and 3 containing activated carbon and calcium oxide, respectively. The purified gas was collected in cylinder by pumping.

2.7.5 Ethanol

Ethanol was recovered after the completion of fermentation process. It was isolated by converting it to an azeotropic mixture and then distilled. The distillates contained ethanol.

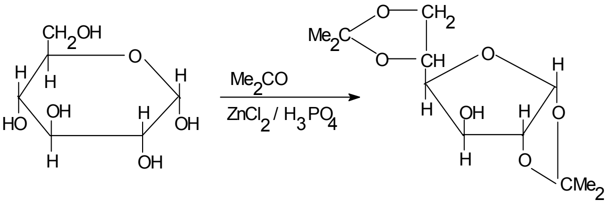
2.7.6 Non-alcoholic soft drink

The alcohol-free mixture was pasteurized at 60°C for half an hour. It was stored for drinking.

2.8. Preparation of Isopropylidene Derivatives

The isopropylidene compounds which are derivatives of sugar were prepared by the standard methods [22-29].

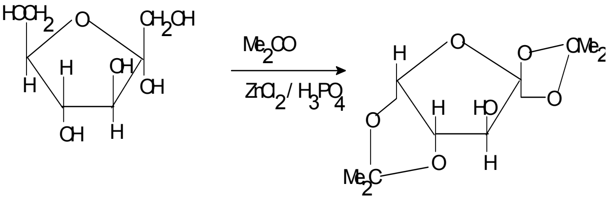
2.8.1 1,2: 5,6-di-o-isopropylidene -α-D-gluco-furanose



Anhydrous ∝-D glucose (37.5g; 0.20 mol) was dissolved in acetone (250 mL) followed by the addition of pulverized anhydrous zinc chloride (30g; 0.21 mol) and phosphoric acid (1.87 mL; 85%). The mixture was stirred for 30 hours at ambient temperature. The undissolved D-glucose (15.45g) was filtered. Filtrate was cooled and made alkaline with NaOH solution (21.25g, 40%). The insoluble inorganic salts were removed and washed with acetone. The concentrated filtrate was diluted with 37.5 mL of distilled water and extracted with chloroform (3 x 37.5 mL). The extract was washed with water and finally concentrated to form a white crystalline compound of 1,2:5,6-di-o-isopropylidine-∝-glucofuranose (diacetone glucose); the product was recrystallized from chloroform and n-hexane (1:2 v/v). Found: C = 54.93%, H = 7.21%, O = 37.86%; Calculated: C = 55.38%, H = 7.69% O = 36.92%. Yield = 90%, m. p. = 109 ^{o}C.

It was partially soluble in acetone, completely soluble in water and chloroform while insoluble in n-hexane.

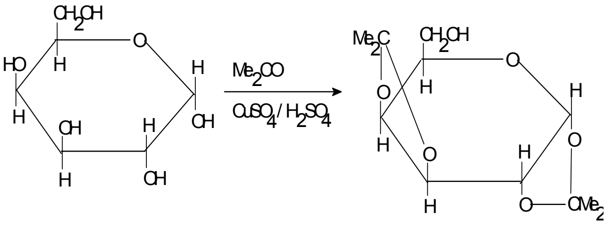
2.8.2 1,2:4,6-di-o-isopropylidene-α-D-sorbofuranose



Anhydrous α-D-fructose (75g; 0.41 mol) was dissolved in acetone (500 mL). The pulverized zinc chloride (60g; 0.44 mol) and phosphoric acid (3.74g; 85%) were added. The mixture was stirred for 30 hours at ambient temperature and then filtered. The filtrate was cooled and the solution was made alkaline with sodium hydroxide (42.5g, 40%). The mixture was filtered and the filtrate was concentrated. The residue was diluted with distilled water (75 mL) and then extracted with chloroform (3 x 75 mL). The extracted compound was washed and concentrated to form white crystalline compound of 1,2:4,6-di-o-isopropylidene-α-D-sorbofuranose (diacetone fructose). It was recrystallized from chloroform and n-hexane (1:2 v/v). Found: C = 55.02 % H = 7.23 % O = 37.75% Calculated: C = 55.38 % H = 7.67% O = 36.92 %. Yield = 89%, m. p. = 102^{o}C.

It was partially soluble in acetone, completely in chloroform while insoluble in n-hexane.

2.8.3 1,2:3,4-di-o-isopropylidene-α-D-galacto-pyranose



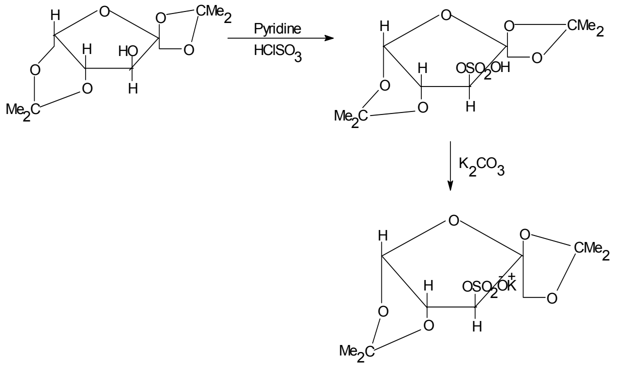
Anhydrous D-galactose (45g; 0.25 mol) powdered anhydrous cupric sulfate (110g; 0.625 mol) and concentrated sulfuric acid (5 mL; d 1.84) were mixed together and then acetone 1L (13.7 mol) was added to the mixture. The mixture was stirred for 24 hours at ambient temperature. Cupric sulfate was filtered and washed with little anhydrous acetone. Filtrate was neutralized with powdered calcium hydroxide (4.7g) until the solution gave congo red coloration. The insoluble inorganic material [$Ca(OH)_2$ and $CaSO_4$] was filtered and washed with dry acetone. The filtrate was concentrated by distillation (it distills at 130-140^{o}C) to form a light yellow oil of 1,2:3,4-di-o-isopropylidene-α-galactopyranose (diacetone galactose).

Found: C = 55.79% H = 7.21% O =37%; Calculated: C = 55.38% H = 7.69% O = 36.92%. Yield = 88%

It was partially soluble in acetone, completely in chloroform and water while insoluble in n-hexane.

2.9. Preparation of Appropriate Salts of Isopropylidene Derivatives

2.9.1 Potassium salt of acid sulphuric ester of 1,2:5,6-di-o-isopropylidene-α-sorbofuranose



Chlorosulphonic acid (116.5g) was added to 500 mL of pyridine at –15°C under continuous stirring and moisture-free environment. After the completion of reaction, 260 g of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose were added (this compound dissolved after 1 hour of stirring). The solution was kept overnight at room temperature (20°C). It was vacuum-distilled for the removal of excess pyridine. The rest was dissolved in a warm saturated solution of 170g potash. The solution was cooled to 0°C which led to the appearance of fine crystalline needles. These were separated mechanically, washed with ice-cold water and recrystallized from calcium carbonate water. The yield was 96% [30] whereas melting point was recorded as 113°C.

Found: C = 37.81% H = 5.38% O = 37.82% K = 9.93%, Calculated: C = 38.09% H = 5.02 O = 38.09 K = 10.31%

It was insoluble in acetone and n-hexane while soluble in water and ethanol.

Similarly, the appropriate salts of 1,2: 5,6-di-o-isopropylidene-α-D-glucofuranose and 1,2:3,4-di-o-isopropylidene-α-D-galactopyranose were prepared by the same procedure as described above.

2.10. Preparation of High Power Fuel

Anhydrous potassium salt of acid sulfuric ester of 1,2:4,6-di-o-isopropylidene-α-D-sorbofuranose (5g) was dissolved in distilled water (5 mL). The solution was heated at 100°C for 10 minutes followed by the addition of ethanol (250 mL; 99.95%), stirring constantly until a clear solution was obtained. It was allowed to cool for half an hr. The product attained was congealed mass of colorless appearance [31-34]. It was soluble in methanol, ethanol and dimethyl sulfoxide while insoluble in acetone, chloroform and ether. It burnt with persistent blue flame.

3. Results and Discussion

The sensible sources are the agriculture materials which include wheat, barley, oat, corn, rye. The initial analytical results (% composition) of these sources and molasses are reproduced in Table 1 whereas the concentrations of macro- and micronutrients are given in Tables 2 and 3, respectively. Fermentation of these sensible sources exhibits the production of liquid protein (LP), ethanol and soft drink. Comparison of the results of sensible sources after fermentation are produced in Table 4 while the results of high fibrous protein (HFP) gained by coagulation after boiling of wort (before starting the fermentation) and CO_2 produced during the fermentation process were recorded as: A = HFP, 3.94%; CO_2, 43%, B = HFP, 3.85%; CO_2, 44%, C = HFP, 4.87%; CO_2, 43.5%, D = HFP, 2.54%; CO_2, 43%, E = HFP, 2.34%; CO_2, 42%, F = HFP, nil; CO_2, 43%. The analytical results of malt husks (solid alcohol product remained after completion of fermentation) are presented in Tables 5 and 6.

The exploited sensible sources showed the following recoveries made during the fermentation: High fibrous protein, 2-4%, which can be used for human consumption in the bakeries, etc. Liquid protein, 0.2-0.3% and can be used in lieu of or in addition to fresh water for cattle. Recovery of carbon dioxide was found to be 43% in fermentation vapors.

Down-stream processing of 5% ethanol into high power fuel (gellified fuel) can be employed for cooking and burning purposes in hilly areas. Ethanol was produced as a power fuel by converting it into 99.95% ethanol. The main physical/chemical properties were compared with commonly-known fuels (Table 7). Ethanol is completely soluble in gasoline, diesel or fuel oil, provided no water is present in the system. The combustible properties of the power alcohol resembled very closely to that of gasoline in internal combustion engines [4,7]. The power fuel.

Table 1. Initial analysis of the sensible sources.

Constituents	Sensible Sources*					
	A	B	C	D	E	F
Crude Fiber (%)	4.5	3.41	1.3	2.2	2.3	-
Total Dietry Fiber (%)	90.55	88.56	84.66	83.22	86.64	54
Soluble (%)	86.05	85.15	83.36	81.02	84.34	-
Insoluble (%)	4.5	3.41	1.3	2.2	2.3	-
Protein (%)	12.00	12.08	12.85	10.91	8.91	-
Total Carbohydrates (%)	77.25	73.23	64.91	71.31	74.54	54
Available Carbohydrates	72.75	69.82	63.61	69.11	72.23	54
Calories (per 100g)	350.70	356.77	367.94	329.08	353.36	216
Fats (%)	1.30	3.25	6.90	1.00	3.20	-
Ash (%)	1.81	1.72	2.90	1.70	1.3	1.37
Moisture (%)	7.56	9.94	13.09	14.70	11.70	16.26

*Sources are A = Barley (Hordeum vulgare), B = Wheat (Tritium aestivum), C = Oat (Avena sativa), D = Rye (Secale cereale), E = Corn(maize) (Zeamays), F = Molasses(non-crystalline sugar). These products are brown, brown, light cream, brown, light yellow and dark brown, respectively. - (Not applicable)

Table 2. Analytical assay of macronutrients in sensible sources (mg%, dry weight)

Macronutrients	Sensible Sources					
	A	B	C	D	E	F
Sodium (Na)	0.43 ± 0.004	0.063 ± 0.001	0.041 ± 0.002	0.32 ± 0.003	0.074 ± 0.001	66.51 ± 0.01
Potassium (K)	6.797 ± 0.061	5.193 ± 0.047	1.631 ± 0.018	4.312 ± 0.032	3.613 ± 0.022	138.322 ± 0.018
Calcium (Ca)	0.456 ± 0.003	0.868 ± 0.007	0.613 ± 0.006	0.723 ± 0.006	0.031 ± 0.003	18.98± 0.02
Magnesium (Mg)	2.785 ± 0.012	1.812 ± 0.023	1.732 ± 0.022	1.413 ± 0.02	2.021 ± 0.014	23.84± 0.03

Table 3. Analytical assay of micronutrients in sensible sources (mg %, w/w dry weight)

Micronutrients	A	B	C	D	E	F
Manganese (Mn)	22.460 ± 0.200	31.480 ± 0.32	18.441 ± 0.192	17.312 ± 0.30	7.651 ± 0.068	2.1 ± 0.21
Iron (Fe)	22.343 ± 0.189	16.281 ± 0.162	17.941 ± 0.178	15.345 ± 0.143	12.691 ± 0.0923	7.7 ± 0.05
Zinc (Zn)	29.061 ± 0.188	30.897 ± 0.281	22.442 ± 0.192	21.385 ± 0.200	22.131 ± 0.214	7.24 ± 0.24
Copper (Cu)	3.261 ± 0.030	2.580 ± 0.023	2.213 ± 0.029	2.100 ± 0.021	1.710 ± 0.009	1.46 ± 0.02
Chromium (Cr)	1.254 ± 0.011	1.280 ± 0.013	0.934 ± 0.011	0.953 ± 0.012	* BDL	0.57 ± 0.012
Cadmium (Cd)	0.253 ± 0.002	0.069 ± 0.001	0.153 ± 0.003	0.092 ± 0.002	0.298 ± 0.003	1.29 ± 0.02
Mercury (Hg)	0.0213 ± 0.001	0.098 ± 0.001	0.003 ± 0.001	0.010 ± 0.001	0.0092 ± 0.0012	0.115 ± 0.001
Lead (Pb)	0.201 ± 0.0023	0.439 ± 0.0039	0.1701 ± 0.0021	0.1231 ± 0.001`	1.300 ± 0.009	BDL
Arsenic (As)	0.108 ± 0.001	0.119 ± 0.001	BDL	BDL	0.91 ± 0.001	BDL
Nickel (Ni)	1.460 ± 0.013	0.048 ± 0.001	1.021 ± 0.021	0.910 ± 0.02	1.790 ± 0.009	BDL

BDL= Below detection limit.

Table 4. Composition of alcoholic product (per 100 mL).

Sample	Liquid Protein (%)	Fat (%)	Ethanol (%)	pH* at 26°C	Ash (%)	Crude Fiber (%)	Soft Drink (%)
A	0.3	Trace	4.7	4.5	—	—	91
B	0.28	Trace	4.5	4.7	—	—	92
C	0.26	Trace	4.4	4.8	—	—	92
D	0.25	Trace	4.4	4.7	—	—	90
E	0.26	Trace	4.2	4.9	—	—	92
F	—	—	4.3	4.7	—	—	—

* Final, — (Not applicable)

Table 5. Composition of malt husks (per 5g).

Sample	Dry Matter(%)	Protein Solid (%)	Fat (%)	Crude Fiber (%)	Ash (%)	Carbohydrates (%)
A	25.42	7.96	1.20	15.94	1.37	15
B	19.42	7.93	1.10	10.91	0.8	17
C	20.41	7.33	1.0	9.81	0.9	9
D	20.10	7.11	0.81	8.99	0.9	13
E	21.31	6.31	1.23	9.92	1.1	14

Table 6. Composition of solid alcoholic product remaining after fermentation (per 50g).

Sample	Dry matter (%)	Crude Protein (solid)* (%)	Ash (%)
A	35.90	16.21	1.59
B	32.88	15.21	1.41
C	32.31	12.31	1.01
D	34.71	11.35	1.61
E	34.00	10.95	1.71

* Including yeast which is itself a protein (45%, w/w)

Table 7. Main Physical/Chemical properties of power alcohol and hydrocarbon fuels.

Property	Ethanol/Power Alcohol	Gasoline	Diesel	Fuel Oil
Formula	C_2H_5OH	C_4-C_{12} Hydrocarbon	C_{14}-C_{19} Hydrocarbon	C_{20} hydrocarbon
Molecular Weight	46.1	100-105 (avg.)	240 (avg.)	N. D.
Composition (Wt. %)				
Carbon	52.2	85-88	85-88	85-87
Hydrocarbon	13.1	12-15	12-15	10-11
Oxygen	34.7	Nil	Nil	Nil
Specific Gravity	0.79	0.72-0.78	0.83-0.88	0.88-0.98
Octane Number	106-111	79-88	N. D.	N. D.
Research	89-100	71-90	N. D.	N. D.
Motor				
Octane Number	0.5	5-10	45-55	NA
Solubility in Water	Infinite	0	0	0
Calorific Value (Kcal/mol)	5048	7700	8738	8795

N.D. = Not determined Avg. = Average NA = Not available

Table 8. Observed IR frequencies of various isopropylidene derivatives* (I, II, III), and salt (IV).

Band Positions (cm^{-1})				
I	II	III	IV	Assignment**
3424	3292	3492	3292	H-bonded OH (s)
2986	2986	2986	2980	$-CH_3$ (s) sym. deformation doublet
2896	2896	2734	2890	C – H (m)
2872	2870	2864	2860	C – O (m)
1458	1455	1458	1455	C = CH_3 (s)
1380	1377	1386	1377	C – $(CH_3)_2$ doublet (s)
--	--	--	1314	$-SO_2$ – O –(v)
1287	1260	1255	1271	O – H bending (m)
1245	1242	1254	1242	C – OH with five-membered ring (m)
--	--	--	1212	$-SO_2$ – O –(s)
1161	1158	1164	1158	C – $(CH_3)_2$ (s)
--	--	--	1038	S = O stretching (s)

Assignment** = m = medium; v = very weak; s = sharp

* I =	1,2:5,6- di -o- isopropylidene - α - D - glucofuranose	II =	1,2:4,6- di-o- isopropylidene - α - D – sorbofuranose
III =	1,2:3,4- di -o- isopropylidene - α - D – galactopyranose	IV =	Potassium salt of acid sulfuric ester of 1,2:4,6- di-o- isopropylidene - α - D -sorbofuranose

as such, cannot be used as diesel substitute because of difference in their combustion properties. As10% blend in conventional fuels, it can be safely used in combustion engines. The power fuel (ethanol; 99.95%) was further converted to high power fuel (equations ix-xii) by treating it with derivative of carbohydrates (glucose, fructose and galactose) prepared by the interaction of these carbohydrates (0.20 mol) with acetone (250 mL) in the presence of $ZnCl_2$ and H_3PO_4 by maintaining the specified experimental conditions. The derivatives, so produced, were further converted into salts by treating them with chlorosulphonic acid and pyridine in the presence of potassium carbonate. The resulting salt was treated with the power alcohol to form gellified material. The yield was quite high and was comparable with one reported by Ohle [30].

Following is the reaction sequence for the fermentation of the sensible sources (SS) and production of high power fuel:

$$\mathrm{S.S} \longrightarrow (C_6H_{10}O_5)_n \cdot nH_2O \qquad (i)$$

$$2\,(C_6H_{10}O_5)_n + nH_2O \longrightarrow n\,C_{12}H_{22}O_{11} \qquad (ii)$$

$$n\,C_{12}H_{22}O_{11} + H_2O \longrightarrow n\,(2\,C_6H_{12}O_6) \qquad (iii)$$

$$C_6H_{12}O_6 \longrightarrow 2\,C_3H_6O_3 \qquad (iv)$$

$$C_3H_6O_3 \longrightarrow CH_3COCOH + H_2O \qquad (v)$$

$$CH_3COCOH + 1/2\,O_2 \longrightarrow CH_3COCOOH \qquad (vi)$$

$$CH_3COCOOH \longrightarrow CH_3COH + CO_2 \qquad (vll)$$

$$2\,CH_3COH + 2\,H_2 \longrightarrow 2\,CH_3CH_2OH \qquad (vlll)$$

$$C_6H_{12}O_6 + 2\,(Me)_2CO \longrightarrow C_{12}H_{20}O_6 \qquad (ix)$$

$$(ix) + ClSO_3H \longrightarrow C_{12}H_{20}O_9S + HCl \qquad (x)$$

$$(x) + K_2CO_3 \longrightarrow C_{12}H_{19}O_8SO^{-}K^{+} + KHCO_3 \qquad (xi)$$

$$(xi) + n\,C_2H_5OH + n\,H_2O \longrightarrow \text{Congealed mass} \qquad (xii)$$

Sensible sources require the conversion of starch $(nC_6H_{10}O_5).nH_2O$ into sugar $(nC_{12}H_{22}O_{11})$ by diastase enzyme [35-39]. The bio-degradation of sugar into glucose is caused by the maltase enzyme (i-iii). The pyruvic acid is an important intermediate of the degradation of carbohydrates by yeast at the same rate, as is the glucose (iv-vi). The reaction proceeds in acidic condition. The glucose molecule is broken into two triose molecules which are hydrated to form methylglyoxal. The triose loses water to form glyoxal which, in turn, is oxidized to pyruvic acid [40-43]. The pyruvic acid is decarboxylated to aldehyde, which on reduction produces ethanol (vi-viii). Glucose was treated with acetone to convert it into its isopropylidene derivative followed by the transformation of this derivative into useful salt, which was used to change power alcohol to high power fuel (ix-xii). The confirmation of isopropylidene derivatives and one of its salt was effected through elemental analysis and IR spectroscopy. The assignments to IR stretchings are given in Table 8 while the IR spectra are reproduced in Fig. 1.

Ethanol molecules (C_2H_5OH) experience hydrogen bonding among themselves in pure alcohol system. This tendency of alcohol showed an interesting transformation to produce high power fuel, i. e., when ethanol came in contact with the derivative of glucose salt, it changed into gellified material. It was possible since gel was frequently described as concentrated solution of a liquid in a solid [44-47]. The liquid system, in this case, was a system of high viscosity that contained structures which were derived from colloidal particles (salts of carbohydrates) exhibiting elastic properties, resisting deformation and frequently possessing a high degree of order showing distinctive properties of three dimensional network. The gel burned with persistent blue flame. The product was similar in its structure and properties to those reported by other workers [30, 31].

Thermal decomposition of high power fuel was carried out in the range of ambient to 500°C. The evolved products were identified by matching the weight-loss with that of the standard products. Table 9 and Fig. 2 present the results of thermal analysis of high power fuels. TG results revealed initial 80% weight-loss corresponding to the elimination of volatile matter (ethanol) present in the network. TG findings were also supported by

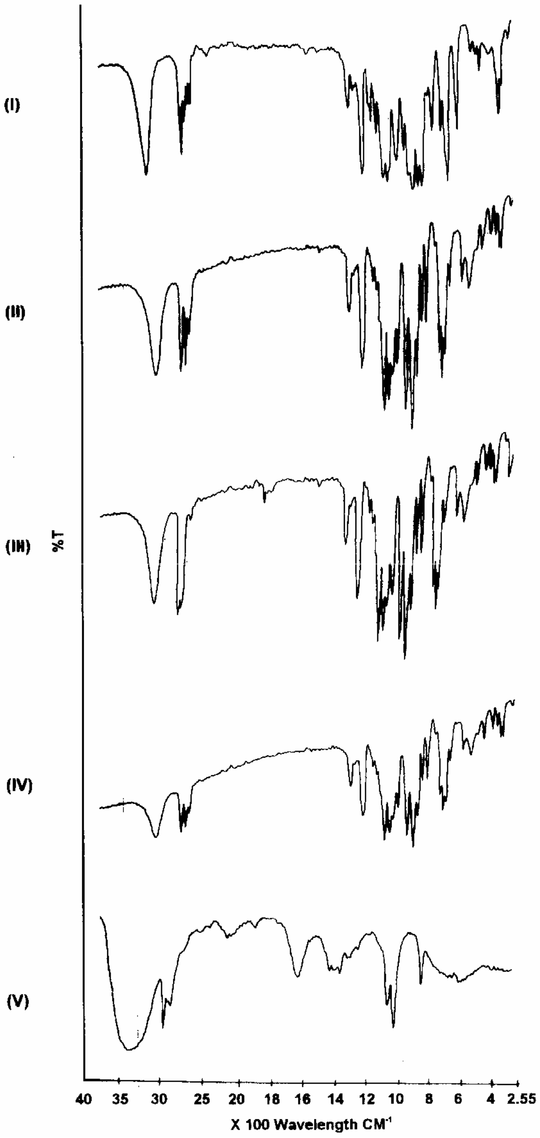


Figure 1. Infrared spectra of isopropylidene derivaties (I-III), one of its salt (IV) and high power fuel (V)

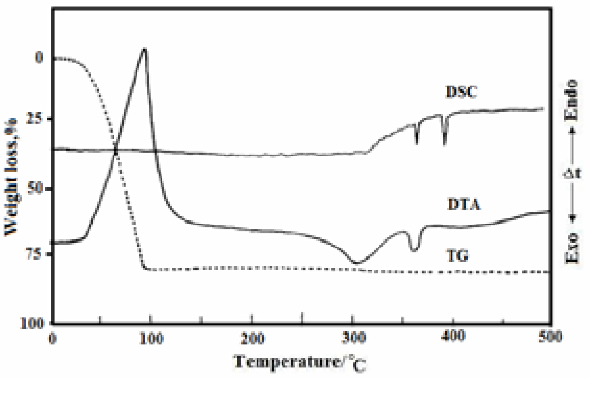


Figure 2. Thermal analysis results of high power fuel

Table 9. Combined TG, DTA and DSC results of high power fuel.

Temperature, °C	Loss in weight (%)	DTA	DSC	Volatile matter	Intermediate
90	80	Endo.	--	$C_2H_5OH + H_2O$	$C_{12}H_{19}O_9SK$
301	--	Exo.	--	CO	K_2SO_4
357	--	--	Exo.	--	--
358	--	Exo.	--	Crystalline transition	K_2SO_4
388	--	--	Exo.	-do-	K_2SO_4

Table 10. Infrared spectral data of high power fuel.

Observed Frequencies (cm⁻)	Band assignment*
3406	Free O-H stretching (b)
2974	$-CH_3$ sym. deformation doublet (s)
2890	$=CH_2$ (b)
1650	C – O – C (b)
1452	$-CH_3$ sym. deformation (m)
1425	SO_2-O- (v)
1386	$=C(CH_3)_2$ sym. doublet (v)
1275	O-H bending
1083	C-O stretching (alcohol)
1044	C-O Primary alcohol (s)
876	CH_3-CH_2- (s)

* b = broad, v = very weak, s = sharp, m = medium

Table 11. Concentration of trace elements in high power fuel.

Trace Element	Concentration (mg%)
Fe	0.13
Cr	-*
Ca	-
Na	0.10
Mg	0.3
K	31.7
Zn	-
Pb	0.2
Cu	-
Cd	-
As	-
Hg	-
Ni	-
Mn	-

*below detection limit

DTA which gave broad volatilization endotherm at 90°C. The subsequent change, however, was not easy to be interpreted by TG curve. DTA result showed an exothermic peak at 301°C which was attributed to the decomposition of the residual mass (evolution of CO) [48].

Furthermore, DTA peak at 358°C was an exothermic change due to the crystalline transition of the potassium salt. DSC result also exhibited two exothermic peaks at 357°C and 388°C. These confirm the energy changes indicated by DTA traces. Combined TG, DTA and DSC results supported the existence of three-dimensional network. IR spectrum displayed the stretching frequencies at 1425 and 876 cm^{-1} which are assigned to the presence of SO_2-O- and CH_3-CH_2- respectively [49-51]. The results are tabulated in Table 10 and the IR spectrum is given in Fig.1. In the trace element study, the result reveals the concentration of potassium at 31.72 mg% (Table 11). It was also evident that the concentrations of toxic metals like lead, cadmium, arsenic and mercury was quite low (in fact, except lead all the toxic metals were below detection limit). This study favors the use of this fuel even under the strict criterion of environmental safety promulgated by environmental protection agencies.

4. Conclusions

The research work presented and discussed in this communication has clearly indicated that the high power fuel, which exhibited elastic properties in resisting deformation and possessed a high degree of order (gel), may be used in a suitable way for burning purposes (burns with pale blue, transparent flame) without sacrificing any of the advantages inherent to the physical condition of a solid body and that chiefly resides in the reduction of shipping, transport, packing and storage costs. The carbon dioxide produced as a result of fermentation process can be stored as a gas and employed in beverages, etc. or it may also be converted into dry ice for cryogenic storage and for the transportation of heat sensitive products. Malt husks and liquid protein, recovered during fermentation, can be used for poultry and cattle feed. The non-alcoholic soft drink can be utilized, after addition of food grade flavor, for drinking purposes. The solid protein has the advantage to be used in bakery products and sold as poultry and animal feed.

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