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Research Article

Biogrease Based on Biochar from Rice Straw and Waste Cooking Oil

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ABSTRACT

Pruning of the very large quantities of rice straw which amount to about 3.28 million ton per year causes a series environmental problem in Egypt. Nowadays intensive attention has been paid to rice straw from the viewpoint of a potential renewable energy source. The utilization of rice straw as thickening and filling agents in the production of lubricating grease constitutes, therefore, one of the major outlets in this area. Accordingly, this work deals with the design of new gel-like formulations based on blends of biochar and Waste cooking oil, which could be potentially applicable as environmentally-friendly lubricating greases. In this respect, the effect of pyrolysis temperatures, ranging 300 to 400°C, on rice straw bio-char yield was investigated. The obtained biochar under different pyrolysed temperature was characterized. The effects of the different ratios of biochar on efficiency of the formulated greases have been studied. The physicochemical and tribological properties of the produced grease are explored according to standard methods. It was concluded that the biogrease based on biochar had superior thermal and tribological properties

Key words: Greases, Lubricant, Waste Cooking Oil, Tribology, Biochar, Rice Straw, Pyrolysis

1. INTRODUCTION

Thermochemical processing of biomass has received significant recent attention as a platform for economically producing energy and chemicals from bio renewable resources [1,2]. Biomass is an important renewable source contributing to the world's economy, sustainability and energy security. In developing countries, the use of biomass is of high interest as these countries have economy largely based on agriculture and forestry. The use of biomass as raw material for bioenergy depends on the state of the art of the technologies which are safe and economical to transform biomass into manageable value-added products [3].

Rice is one of the most abundant crops in Egypt, 2 million feddans with an average production of about 6.12 million tons per year and 9.5 tons per hectare in 2005.It is mainly cultivated in northern east part of the country especially in Kafr El- Sheikh, Al- Sharkia and Al- Dakahlia governorates. In Egypt, processing of rice in the river Nile Delta yields large amounts of rice straw as residue. About 20 % was used for other purposes such as ethanol, paper and fertilizers production as well as fodders [6] and the remaining part was left on the field for burning within a period of 30 days to get quickly rid of leftover debris. The resulting emissions significantly contribute to the air pollution called the "Black Cloud [4,5].

The first grease that been formulated were bio-based during 1400 B.C. which tallow was utilized to lubricate chariot wheels. From the year of 1859, there was petroleum grease were manufactured. A number of studies have been reported on various aspects of mineral oil based grease characterization to understand the fundamental aspects of grease lubrication [6-9]. Recently, due to increasing in petroleum prices and its pollution; thus, to decrease the pollution, the utilization of alternative and environmental friendly grease is one of the solutions to overcome the problems. Instead of using mineral oil as base oil to produce grease, vegetable oil is believed to be a potential source to meet the purpose. The use of bio-based oleochemicals as lubricant fluids, metalworking fluids and greases has increased dramatically. There were many researchers doing researches in formulating biobased grease [10-12]. Florea et al[13] have studied the effect of different base fluids on the properties of biodegradable greases. El-Adly et al. [14] described the preparation of greases using jojoba constituents and some fatty by-products

In this respect, efficient production of lubricating greases from renewable biomass has been entreatingly required in the present mass-consumer society. Since pyrolysis is the first step for any thermochemical conversion processes, sound understanding of the biomass pyrolysis process can give rise to the improvement of its conversion processes. Accordingly, the objective of this work is to produce biogrease from bio-char obtained from pyrolysis of the rice straw and waste cooking oil.

2. MATERIAL AND METHODS

2.1. **Materials**;

Waste cooking oil was obtained locally as the biodegradable fluids for preparing biogrease under investigation. It was purified and filtered using superfast M2FF bleaching earth (highly active acid bleaching earth, AMCOL). Waste cooking oil after this treatment was designated PWCO. The physicochemical properties of this oil were investigated elsewhere [15]. Stearic acid was used as source of soap thickener. Calcium hydroxide used as alkali for saponification step. Rice straw was obtained locally from El-Beheria governorate (Nile Delta region). Commercial Calcium grease designated G4 was provided by Co. Operation Petrol.

2.2. Pyrolysis of the rice straw

Before pyrolysis, rice straw was cutting and milling to a diameter about 1mm. After that, the sample was dried in a vacuum oven at 80 ^oC for 24 hours. Slow pyrolysis experiments of rice straw were carried out at temperatures 300. 350 and 400^{0}C for different time in the autoclave patch process to investigate the effects of temperatures on the pyrolysis yield. This process was fitted with a nitrogen purge (1 L/min flow rate) and a thermocouple for temperature measurement. The residual bio-char particles were collected as total yield of the pyrolysis process. The total yield was determined by the difference between the weight of sample before and after the pyrolysis experiment. The bio-oil was collected through the condensation system. Mass yield of bio-char was ranging 42.2% and 53.0%. Worth mentioned, the pyrolysis in this study agrees well with the procedure of work reported [16-18].

2.3. Rheological characterization

The rheological behaviour of the prepared biogreases was carried out at temperature 90, 100,110 and 120^{o}C. At least two or triplicates of each test were performed on fresh samples. This behaviour was carried using Brookfield programmable Rheometer HA DV-III UITRA used in conjunction with Brookfield software, RHEOCALC V.2. Through RHEOCALC, all Rheometer functions (rotational speed, instrument % torque scale, time interval, set temperature) are controlled by a computer.

2.4. Grease preparation

Three grades of Bio grease designated G1, G2 and G3 were prepared based on PWCO, lime, biochar **,** colophony , natural rubber and octyl amine as mentioned in **Table 1**. Worth mentioned, the biochar used in the prepared greases under investigation is obtained at temperature 300^{0}C (less bio-oil obtained). The prepared greases were made in batches of one liter in an open kettle with a capacity of 2 liter, fitted with a mechanical stirrer . The saponification process was performed on a mixture of PWCO and stearic acid (1: 1 volume ratio) with calcium hydroxide, at 150-170°C. The reaction time for each saponification process to achieve a soap structure was found to be dependent on the type of constituent. After the completion of the reaction, the reaction mixture was cooled gradually while the biochar and BWSO were added to get NLGI-2. Physicochemical properties of the prepared greases were determined according to standard method.

2.5. Friction co-efficient Measurement by Pin on Disc Method

The tribological properties of the prepared biogreases were evaluated using pin on disc apparatus which is fabricated as shown in **Figure 1** at room temperature. The chemical composition of both Pin and disc were presented in **Table 2.** In this respect , The test specimens (Pin) were AISI1023 steel with diameter of 10mm and HRC about 20.5. However, the Disc was manufactured from Wear resisting steel (Hardox 600) with diameter of 10 cm with HRC about 59.5. Pin -on-disc experiments were carried out at different times, speed 60 rpm, and load 358.065 N, using the grease samples. The weight losses in pin were calculated and the corresponding friction coefficients were determined for each sample. In addition, the weld loads of the prepared biogreases were carried out using four ball test according to ASTM D-2596 method.

3. RESULT AND DISSCUSSION

3.1. Composition of the rice straw

Chemical composition of the rice straw under investigation is given in Table 3. Data presented in this table show that the lignocellulose is the main component of rice straw, which is formed compact structure of cellulose in close association with lignin-substituted phenyl propane three dimensional polymers which are held together by ether or carbon bonds (14.5%) and silica (14%).These results are in agreement with other studies on rice straw composition (3,4 and18). In addition, the main mineral elements are Potassium, phosphorus, calcium and magnesium. Moreover, there are traces from the elements cobalt, copper, and manganese. It may be concluded that the chemical composition of rice straw depend on the species, climate and geography location.

3.2. Effect of temperature on biochar yield

The effect of final pyrolysis temperature on bio-char yield is shown in Table 4. The bio-char yield significantly decreased as the final pyrolysis temperature was raised from 300-400°C. The highest bio-char yield was 48% obtained at the temperature of 300°C and the lowest bio-char yield was 35% obtained at the temperature of 400°C. Visual texture of the lubricating greases containing biochar shows that the smooth properties at all temperatures and this reveal that the suitability of all biochar obtained as thickening and filling agents for lubricating greases under investigation.

3.3. **Grease evaluation**

The preparation of lubricating grease is a complicated trial-and error process in which the optimization of the ingredients the reaction scheme are to achieve the desired grease consistency. So, the development of lubricating grease with the right consistency requires stringent optimization of components and preparation scheme. Important performance properties such as Rheology, penetration, oxidation, oil separations and dropping point are largely dependent on the grease hardness and its ability to maintain a stable lubricating film at the metal contact zone. Accordingly, Three biobased greases (G1, G2 and G3) were prepared based ingredients percentage as presented in Table 5.

Experimental data reported in this Table 5, show the results of the penetration, oxidation stability, and dropping point tests for the obtained biogreases. These tests show that the no difference of penetration values between unworked and worked (60 double strokes) of biogreases. Results obtained for G1, G2 and G3 in this table were better to those obtained for the commercial grease G4. Also, dropping point and oil separation for the prepared greases are showed remarkable improved compared with G4. On the other hand, G4 had better oxidation stability.

It may be point out that the specifications of all prepared bio-greases meet with the NLGI-2. In the mean time, G1, G2 and G3 have thickening power over G4. This indicates that the role of the biochar using in the preparation of biogreases. In general, data in Table 5 show that the biogreases preparation is complicated trial-error process in which the optimization of the fluid (PWCO) and the chemical compositions of this oil are critical to achieve the desired grease property. The percentage of biochar and its composition are playing important roles in physicochemical characterization of the prepared biogreases.

3.4. Rheological Behavior of Selected Greases Compared with Commercial.

Mathematical models , Heshel-Bulkley, Bingham and Casson, was explored of prepared greases using linear and non-linear computer regression programs (Rheocalc ,V2.7) at different temperatures as presented in Table 6 . It was found that Heshel-Bulkley, showed the best rheological equation that fits the experimental data reasonably well as presented in Table 6. These data reflected by regular decreasing in consistency index with the increasing of temperature. Such improvement in consistency index may be attributed to the enhancement activity for biochar constituents. On the other hand, the all greases showed plastic flow .

3.5. Tribological properties of prepared biogreases compared with commercial

The effect of biochar concentrations on the friction co-efficient and weld load of prepared greases (G1, G2 and G3) are presented in Table 7. The friction reduction and extreme pressure properties of these greases could be remarkably improved by increasing concentrations of biochar compared with, G4, commercial one. This reveals that the active components of the biochar have chemical interaction with the Ca- soap or PWCO. They are primarily dispersed in the PWCO in the grease matrix and start acting during the metal-rubbing process. During this process, biochar molecules could be undergo chemical transformation at the metal contact zone and develop a stable tribochemical film to protect against frictions. This is because the polar PWCO and biochar compete for the metal surfaces, and a higher proportion of biochar will increase its rate of diffusion to the metal surface due to reduce the friction. In this respect, the G1, G2, G3 and G4 greases were tested in a four ball machine where a rotating ball slides over three stationary balls using ASTM-D 2596 procedure; The weld load data for the these greases are 175, 195 250 and 150 Kg, respectively **Table** 7. These results indicate that the prepared biogreases containing biochar exhibit remarkable improvement in extreme pressure properties compared with commercial grease. This may be attributed to the synergistic effect of the complex combination among ca-soap and biochar molecules such as, silca, phosphrous, Mg^{2+} , K^{+}, Co^{2+}, Ca^{2+}, Mn^{2+} . They react with the surface to form protective films which prevent metal to metal contact and the consequent scoring or welding of the surfaces. The biochar could be intended to improve the performance of the lubricating greases. This view introduces the key reasons for the improvements of the load-carrying properties as shown in Table 7

CONCLUSION

In this study, pyrolysis of rice straw was carried out using a autoclave in patch process. The highest bio char yield of 58% was obtained at an optimum pyrolysis temperature of 300°C with smooth texture less bio oil. Biogrease composed from biochar and waste cooking oil has promising future as reliable lubricating greases for plenty of application. Biochar able to absorb oil and hold the fluid. The obtained data concerning penetration, dropping point and oil separation leads to biochar can be used a good thickener for lubricating greases. The application of waste cooking oil and rice straw in such greases is a wise way to decrease pollution as well as to preserve the environment.

Table 1
Ingredients of the prepared biogreases

Type of Grease Ingredient, Wt%	G1	G2	G3
Purified waste cooking oil	81.0	81.2	81.4
Stearic acid	12.0	8.0	4.0
Calcium hydroxide	1.2	1.0	0.8
Biochar @ 300^{0} C	3.0	7.0	11.0
Colophony (resin)	2.0	2.0	2.0
Natural rubber	0.5	0.5	0.5
Octyl amine	0.3	0.3	0.3

Table 2
Chemical composition of the Pin and Disc

Element, %	Pin	Disc
C	0.23	0.47
Ni	0.10	2.5
Mo	0.0117	0.7
Cr	0.10	1.2
Fe	98.1	95.6
Mn	0.71	-
P	0.029	-
S	0.021	-
Cu	0.30	-
Si	0.19	-

Table 3
Chemical composition of rice straw

Component	Percentage (%)
Moisture	22
lignin	14.5
Cellulose	34
Nitrogen free extract	42
Ash	19.5
Silica	14
Calcium	0.17
Phosphour	0.10
Potassium	1.20
Magnesium	0.11
Sulfur	0.08
Cobalt	0.05(mg/kg)
Copper	5(mg/kg)
manganese	4(mg/kg)

Table 4
Effect of temperature on the biochar yield

Temperature, ^{o}C	300	325	350	375	400
Weight gram	100	100	100	100	100
Biochar, yield wt %	48	45	40	38	35
Silicon oxide	12-13	12-13	12-13	12-13	12-13
Visual texture	Smooth	Smooth	Smooth	Smooth	brittle

Table 5
Physicochemical properties of the prepared greases compared with commercial

Test	**Prepared biogreases and commercial**				**Test method**
	G1	**G2**	**G3**	**G4**	
Penetration at 25^{o}C **Unworked**	295	275	260	265	\ ASTM D-217
worked	294	275	260	270	
Dropping point, ^{o}C	155	165	190	100	ASTM D-566
TAN, mg KOH/gm, @72h	0.1	0.1	0.2	0.1	ASTM D-664
Oil separation, Wt%	0.5	0.3	0.1	3.3	ASTM D-1724
Oxidation Stability at, 99^{o}C, 96h, pressure drop, psi	3.1	3.2	3.1	3.4	ASTM D-942
Copper Corrosion 3h/100^{o}C	Ia	Ia	Ia	Ia	ASTM D-4048

Table 6
Viscoelastic parameters for selected prepared greases, of Herschel Buckley at different temperatures

Test	90 °C				100 °C			
	G_1	G_2	G_3	G_4	G_1	G_2	G_3	G_4
Consistency index	27355	28132	29413	24552	1186	9840	19000	1095
Yield stress, D/cm²	72.6	80.9	86.6	65.2	60.0	68	70	60.5
Flow Index	0.42	0.35	0.33	0.3	0.52	0.46	0.41	0.37
Confidence	98.5	98.9	100	100	99.6	99.9	100	100
Test	**110 °C**				**120 °C**			
	G_1	G_2	G_3	G_4	G_1	G_2	G_3	G_4
Consistency index	618	2371	3510	513	871	1892	2121	501
Yield stress, D/cm²	28.7	31.2	35.8	37.5	19.2	21.5	23.1	28.7
Flow Index	0.64	0.61	0.56	0.4	0.89	0.83	0.78	0.73
Confidence	99.8	100	100	100	98.9	100	100	100

Table 7
Tribological properties of prepared biogreases compared with commercial

Biogrease	Friction co-efficient	Weld load, Kg
G1	0.17	175
G2	0.15	195
G3	0.12	250
G4	0.21	150

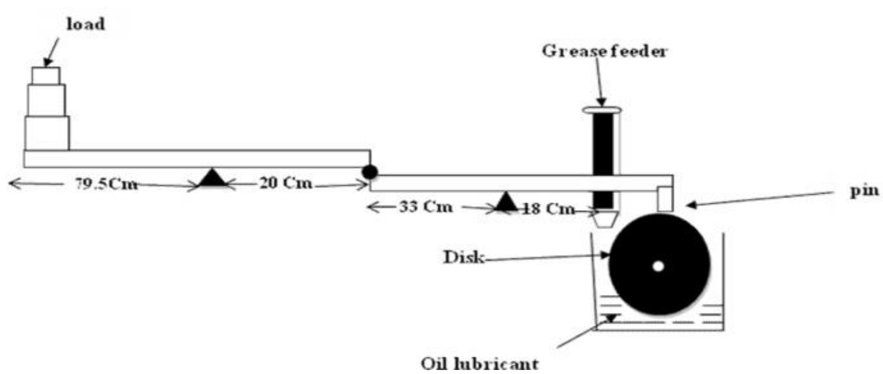

Figure 1
Schematic view of the pin on disc apparatus

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