Feasibility of Sea and Coconut Shells as Substitute to Barium Carbonate (BaCO_3) in Small Scale Foundry and Heat Treatment Shop in Nigeria

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Barium Carbonate (BaCO_3) is commonly used as an energizer in pack-carburization. Investigation was therefore carried out to establish the suitability of sea shell and coconut shell as energizers in pack-carburization of mild steel. Samples were carburized at 950°C in carburization compounds containing charcoal and energizing materials at predetermined proportions. The results obtained showed that sea shell was a more effective energizer than the coconut shell and compared favourably with barium carbonate. Sea shell showed 82.5% efficiency compared with BaCO_3 and 134.7% with limestone (CaCO_3) at 950° carburizing temperature. It was found that 30% sea shell addition to charcoal gave optimal carburization case depth which was 2.8 times the values obtained from 100% charcoal. However, there was no significant difference between 100% charcoal and compounds containing various proportions of coconut shell in the carburizing kinetics.

KEY WORDS: pack-carburization; energizers; barium carbonate; sea shell; coconut shell; heat treatment; foundry shop; substitute.

1. Introduction

Barium carbonate (BaCO_3), Sodium carbonate (Na_2CO_3) and Potassium carbonate (K_2CO_3) have been added to charcoal to enhance carburization. These carbonate salts are generally referred to as energizers.^{1,2)}

In many developing countries, small scale foundries and heat treatment shops have abundant charcoal derived from the burning of fire wood. The charcoal is normally disposed of as a waste product and therefore can be sourced free or at minimum cost to the user. In contrast to charcoal, energizers (BaCO_3 , Na_2CO_3 , K_2CO_3) are difficult to source locally and are often imported. The foreign exchange requirement for the importation of these important raw materials hinder the development of small scale foundry and heat treatment shops. It is therefore necessary to find an acceptable alternative energizer(s) to encourage the expansion and growth of the foundry industries in Nigeria and other developing countries.

Possible sources of energizers in many parts of Nigeria include lime stone (CaCO_3), sea shell and coconut shell. It is of interest to note that sea and coconut shells are waster products from agricultural crops and can be obtained without significant cost in most of the riverine areas and equatorial forest zones. Also, they are renewable sources unlike rock mineral energizers.

Lime stone involve mining processes which make it an expensive source. The focus is therefore placed on sea

and coconut shells as substitute energizers. Research work was carried out to characterise sea and coconut shells for possible use as energizers in small scale foundries.

2. Background

Coconut shell is classified as a polysaccharide with molecular formula $\text{nC}_6\text{H}_{12}\text{O}_6$ and chemical composition, on dry basis, consisting of approximately 36.51% lignin, 33.61% cellulose, 29.27% pentosan and 0.61% ash.³⁾ About three million tons are produced annually in growing countries and only a very small portion is collected commercially. According to Woodroof,³⁾ coconut shell is similar to hardwood and contains little or no oil and resinous matter. Sea shells, on the other hand, are the calcified covering of most mollusks and composed of conchiolin which is mainly a mineral salt of calcium carbonate (CaCO_3) with traces of magnesium carbonate (MgCO_3), negligible amount of calcium phosphate. Analyses of the sample collected at Calabar, Cross River State, Nigeria gave the following composition: 4.07% SiO_2 , 0.08% Al_2O_3 , 0.08% Fe_2O_3 , 88.46% CaCO_3 and 0.96% MgO .⁴⁾ One observes that the coconut shell is composed mainly of organic compounds while the sea shell contains inorganic compounds. No information is available in the literature on the use of shells as energizers.

Pack carburization or solid carburizing is accom-

plished by placing steel parts in a box filled with charcoal lumps and other additives. The carburization temperature is between 900 and 950°C and entrapped air within the charcoal lumps reacts to form carbon monoxide (CO):

Carbon monoxide is unstable at the process temperature and thus decomposes according to the Eq. (2)

The atomic carbon (C^0) is quickly absorbed at the metal surface and diffuses into the metal. The carbon dioxide reacts with more charcoal to produce more carbon monoxide:

The process is repeated with increase in the surface concentration of absorbed atomic carbon. The metal is therefore carburized by the gas produced from a solid carburizer.

The amount of atmospheric oxygen in a charcoal packing can vary and may be insufficient to produce enough carburizing gas (CO). This makes it necessary to provide more oxygen to enable the production of sufficient CO. From Eq. (3), the amount of CO can be increased by reacting CO_2 with charcoal.

The chemistry of most carbonates reveals that these carbonates decompose to metal oxides and carbon dioxide on heating to high temperatures. From available data^{1,5)} the minimum decomposition temperature of the commonly available carbonate falls below the process temperature of carburization. It is therefore possible to generate CO_2 by decomposing carbonate salts in the carburizing compound. This gas will react with charcoal according to Eq. (3). The simplicity of the decomposition process and the relative abundance of carbonate salts favour the use of carbonates as energizers.

In Nigeria, sea and coconut shells are abundant, especially in the riverine areas and equatorial forest zones. Their utilization as industrial raw materials will encourage large scale farming of both mollusks and coconut trees. Economically, the shells will be cheaper than mined carbonates such as CaCO_3 , BaCO_3 and Na_2CO_3 .

3. Experimental Procedure

3.1. Materials

The mild steel used for the investigation was obtained from Jos Steel Rolling Company, Jos. The steel was classified as RST37 with the following composition:

C	Si	Mn	P	S	Cr	Ni	Cu	Fe
0.15	0.21	0.51	0.022	0.006	0.02	0.02	0.07	Balance.

The above composition is closely approximated by SEA 1015. Sea and coconut shells were obtained from Cross River State, Nigeria. The carburizing box measured 80 × 80 × 70 mm and was made of heat resistant steel.

An electric muffle furnace type OH85TR made in Hungary was used. Vickers hardness testing machine

Table 1. Carburizing compounds using sea shell as energizer.

Compound	Composition
1	100 % charcoal + 0 % sea shell
2	90 % charcoal + 10 % sea shell
3	80 % charcoal + 20 % sea shell
4	70 % charcoal + 30 % sea shell
5	60 % charcoal + 40 % sea shell
6	50 % charcoal + 50 % sea shell

Table 2. Carburizing compounds using coconut shell as energizer.

Compound	Composition
1	100 % charcoal + 0 % coconut shell
2	90 % charcoal + 10 % coconut shell
3	80 % charcoal + 20 % coconut shell
4	70 % charcoal + 30 % coconut shell
5	60 % charcoal + 40 % coconut shell
6	50 % charcoal + 50 % coconut shell
7	0 % charcoal + 100 % coconut shell

model MHT.1 made by Matsuzawa Seiki Company of Japan was also used. Microstructural observations were made using Olympus optical microscope.

3.2. Procedure

Hardwood charcoal and the shells were ground and sieved to particle size of 80 % finer than 425 μ . The charcoal and the shells were mixed at predetermined proportions as shown in **Tables 1** and **2**. The mild steel rods were cut into 30 mm length and thoroughly washed in acetone and allowed to dry. The bottom of the carburizing box was covered with a layer of the carburizing compound chosen from **Tables 1** and **2**. A single specimen was placed in each box and the remaining space was filled with the carburizing mixture. The box was covered with a lid and sealed with fireclay to prevent infiltrate air from entering the box during carburization. The box was then placed in the central zone of the furnace which was found to have a constant temperature. Carburizing times of 2, 4, 6 and 8 h were used. At the end of each test, the box was removed from the furnace and quenched into water at room temperature (27°C). Each set of test was repeated at least three times. The samples were prepared for hardness and microstructural analysis.

4. Results and Discussion

4.1. Effect of Energizer Concentration on Carburization Kinetics

Carburization kinetics greatly depended on the concentration of the carburizing medium at a constant temperature, holding time and a fixed distance from the surface of the sample. The effect of varying the amount of the sea and coconut shells is presented in the following section.

The hardness profile of the uncarburized steel was taken at 0.2 mm interval and the mean was found to be Hv 223.95 with a standard deviation of 0.60. The profile

was taken from the edge to 4 mm depth. **Table 3** is a summary of the results of hardness measurements on carburized samples using charcoal and sea shell. In general, it could be observed that initially, as the amount of sea shell increases, the rate of carburization also increases. It is also observed that an optimal value occurred at 30 % sea shell and 70 % charcoal. Above 30 % sea shell addition, the hardness values dropped.

Table 4 summarises the results using various concentrations of coconut shell and charcoal. It can be seen that there is no significant increase in the hardness values, at any given depth, due to increase in the coconut shell concentration. At 100 % coconut shell, the hardness profile was not different from those obtained at 100 % charcoal. This result indicates that coconut shell was not effective as an energizer but merely behaved as charcoal, thus confirming the statement by Woodroof³⁾ that coconut shell is similar to hardwood.

4.2. Influence of Holding Time on Carburization Rate

The holding time in the furnace influenced the carburization characteristics of the steel. Displayed in

Table 3. Effect of concentration of sea shell on the hardness profile of carburized mild steel, RST37 at 950° for 2 h.

Distance (mm)	Hardness values (Hv) at concentration of sea shell (%)					
	0.0	10.00	20.0	30.0	40.0	50.0
0.2	618	705	763	804	798	775
0.4	575	644	725	775	763	757
0.6	543	598	657	746	700	675
0.8	523	547	583	661	652	622
1.0	490	523	547	639	606	579
1.2	481	505	540	606	547	543
1.4	478	490	520	554	533	530
1.6	457	481	502	520	520	517
1.8	422	478	490	514	502	496
2.0	371	547	483	505	487	484
2.2	341	427	476	490	484	481
2.4	312	371	465	481	478	470
2.6	294	341	444	470	457	451
2.8	260	312	406	465	418	400
3.0	244	294	373	444	396	481
3.2	242	260	341	406	364	351
3.4	240	244	312	371	341	328
3.6	240	242	269	323	315	270
3.8	238	240	255	270	252	250
4.0	238	240	242	251	244	240

Table 5 is the result obtained by holding the samples at 2, 4, 6 and 8 h in the furnace. At a fixed concentration of additives and case depth, the hardness value increased with the holding time. Similar observation was made with respect to coconut shell compounds.

In order to further understand the dissimilar behaviour of the sea shell and the coconut shell as energizers, possible reaction mechanisms affecting the compound are presented in subsequent sections.

4.3. Reaction Kinetics and Mechanism

The above results show that sea shell enhances the carburization kinetics of mild steel while coconut shell was not quite effective as an energizer. The difference in the effectiveness of the two compounds as energizers could be due to the reaction mechanism occurring in both materials. The extent to which these mechanism favour Eqs. (2) and (3) will result in increased carburization rate.

Sea Shell Reactions: The major reactions from the sea shell include the following:

- (i) Decomposition of the carbonates

Table 4. Effect of concentration of coconut shell on the hardness profile of carburized mild steel, RST37 at 900°C for 2 h.

Distance (mm)	Hardness values (Hv) at concentration of coconut shell (%)						
	0.0	10.0	20.0	30.0	40.0	50.0	100.0
0.2	618	618	618	622	622	618	631
0.4	575	579	575	579	575	579	583
0.6	543	547	543	547	543	547	547
0.8	523	523	527	523	527	523	523
1.0	490	490	493	490	493	490	502
1.2	481	484	481	484	481	484	490
1.4	478	478	476	478	476	478	478
1.6	457	459	454	457	459	457	457
1.8	427	427	425	427	425	427	441
2.0	371	373	371	372	371	373	427
2.2	341	344	343	344	343	344	400
2.4	312	312	314	312	314	312	375
2.6	294	294	291	293	291	294	353
2.8	260	270	260	270	260	270	341
3.0	244	245	247	245	247	245	320
3.2	242	245	242	245	242	245	301
3.4	240	244	242	244	242	244	282
3.6	240	242	242	242	242	244	269
3.8	238	242	240	242	240	242	256
4.0	238	240	240	242	240	242	242

Table 5. Effect of holding time on the carburization rate of mild steel (hardness profile)* at 950°C.

Distance (mm)	2 hr						4 hr						6 hr						8 hr					
	(% Sea shell)						(% Sea shell)						(% Sea shell)						(% Sea shell)					
	0	10	20	30	40	50	0	10	20	30	40	50	0	10	20	30	40	50	0	10	20	30	40	50
0.2	618	705	763	804	798	775	690	769	780	862	810	798	705	869	966	1149	1034	990	876	958	1025	1203	1119	1007
1.0	490	523	547	639	606	579	523	583	622	730	720	675	547	610	659	999	756	752	618	829	856	1016	958	912
2.0	371	457	483	505	487	484	341	476	496	547	533	502	320	470	490	606	579	533	440	533	540	842	769	543
3.0	244	294	373	444	396	481	244	341	381	425	418	396	263	402	432	502	444	436	371	422	377	492	478	444
4.0	238	240	242	251	244	240	236	240	242	250	244	241	240	251	298	371	341	280	240	251	261	321	285	271

* Hardness values are in Vickers Hardness number (Hv).

Fig. 1. Graphical determination of case depth using hardness profiles and distance data for different carburizing compound after 2 hr at 950°C.

(ii) Oxidation of charcoal (oxygen deficient condition)

(iii) Decomposition of carbon monoxide

The ease of generation of CO_2 in Eq. (4) will result in the eventual increase of the concentration of atomic carbon (C^0) as shown in Eq. (6). From the above argument, one would expect a direct linear relationship between the concentration of sea shell and the degree of carburization. However, it was observed that an optimum carburization occurred at 30% sea shell addition. Equations (5) and (6) imply that the Bourdourd reaction equilibrium must be satisfied at the reaction temperature. From Eq. (5):

and
$$K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} \quad \text{.....(7)}$$

where K_p is the equilibrium constant.

A plot of the average case depth against the concentration of sea shell is presented in Fig. 1. From Table 3 and Fig. 1, the hardness values are observed to decrease as the concentration of the sea shell exceeds 30%. This could mean that the furnace atmosphere is highly rich in CO_2 , giving rise to decarburization. On the other hand, below 30% additions, the furnace atmosphere could be deficient in CO and hence the slow carburization kinetics. Also from Fig. 1, longer holding times gave higher values of case depths at all com-

positions of the carburization compound.

Coconut Shell: Two possible reactions can be presented for coconut shell at the reaction temperature.

(i) Dissociation of the polysaccharides

(ii) Gasification of the polysaccharides

Equation (8) will merely increase the overall carbon content of the carburizing compound. Since the carbon concentration in the charcoal (85–98% C)⁶⁾ can be considered supersaturated, further increase of the carbon content due to the dissociation of the polysaccharides will not significantly influence the reaction rate, if other conditions remain constant. This analysis confirms the result shown in Table 4.

Equation (9) would support increased carburization kinetics but was not thermodynamically favoured at the process temperature. It was further observed that the tests with coconut shell generated severe scaling problem on the specimen and the carburization box. This observation supports the production of H_2O instead of H_2 and further confirms that the dissociation reaction was favoured at the reaction temperature.

4.4. Case Depth Determination

Graphical: Figure 2 is a plot of hardness profiles against distance at various compositions of the carburizing compound. The graphical determination of the case depth was based on 50% martensite, 50% pearlite phases commonly taken at Hv 550 as shown in Figs. 1 and 2. Values of case depth at 2, 4, 6 and 8 h are displayed in Tables 6 and 7. The case depth is maximum at 30% sea shell and increases with holding

Fig. 2. Effect of holding time on the carburizing kinetics using 30 % shell at 950°C.

Table 6. Case depth (mm) measured at HV550 and 950°C carburization temperature.

% Seal shell	0	10	20	30	50
Case depth (mm)	0.55	0.90	1.10	1.45	1.30

Time = 2 hr.

Table 7. Case depth measured at HV550, 900°C carburizing temperature and different holding time.

Composition of carburizer	30 % Sea shell				100 % Charcoal	100 % Coconut Shell
Holding time (hr)	2	4	6	8	8	8
Case depth (mm)	1.45	1.95	2.60	2.80	1.10	1.10

time. It is of interest to note that the case depth obtained at 100 % charcoal coincided with that of 100 % coconut shell after 8 h of carburization. The hardness profiles in both cases were similar.

Analytical: Carburizing rate can be analyzed using an expression derived from Fick's first law of diffusion for the rate of increase of the case depth, l . The flux of carbon atom diffusing through the steel in the x -direction can be given by:

$$J = (J_s) = -D_s \left(\frac{\partial C_s}{\partial x} \right) \quad (10)$$

Where J_s : flux of carbon atom ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$)
 D_s : Diffusion Coefficient ($\text{cm}^2 \cdot \text{sec}^{-1}$) of C in Fe
 C_s : Concentration of carbon ($\text{mol} \cdot \text{cm}^{-3}$).

For semi-infinite medium, the carbon concentration profile can be approximated as linear, thus leading to the integration

$$J_s \int_0^1 dx = - \int_{C_0}^{C_1} D_s dC_s \quad (11)$$

Where C_0 : carbon concentration at $x=0$

C_1 : carbon concentration at $x=1$

x : distance from edge of specimen.

At steady state, Eq. (11) can be rearranged to obtain the instantaneous flux at a given depth, l .

$$J_s = \frac{1}{l} \int_{C_0}^{C_1} D_s dC_s \quad (12)$$

Under the above condition $\int_{C_0}^{C_1} D_s dC_s$ is equal to a constant, θ .

Therefore

$$J_s = \frac{\theta}{l} \quad (13)$$

The flux is proportional to the growth rate of the case depth, l .

$$J_s \propto \frac{dl}{dt} \quad (14)$$

or

$$\frac{\theta}{l} \propto \frac{dl}{dt} \quad (15)$$

on integration

$$\int_0^1 l dl = \int_0^t \theta' dt \quad (16)$$

or

$$l^2 = 2\theta'_t$$

and

$$l = \sqrt{2\theta'_t} \quad (17)$$

Here θ' is a constant with units $\text{cm}^2 \cdot \text{sec}^{-1}$ and can be taken to approximate the diffusivity of the medium.

The diffusivity (D) of carbon in austenite at 950°C is

Table 8. Comparative values of different energizers.

Energizer	30 % Sea shell	10 % Marble	20 % Dolomite	20 % Lime stone	20 % BaCO ₃
Case depth (mm)	1.45	0.68	0.36	1.08	1.76
Efficacy*	2.64	1.24	0.65	1.96	3.2

* Efficacy = $\frac{\text{case depth with energizer}}{\text{case depth at 100 \% charcoal}}$
(Time and temperature are kept constant.)

given as $1.8 \times 10^{-7} \text{ cm}^2/\text{sec}$ and $1.3 \times 10^{-7} \text{ cm}^2/\text{sec}$ by Geiger and Poirier⁷⁾ and Weast,⁵⁾ respectively. From Eq. (17), the average value of θ^1 was determined to be $2.1 \times 10^{-7} \text{ cm}^2/\text{sec}$ using data and case depths for 100 % charcoal samples. This value of θ^1 is in agreement with published value for D for carbon diffusion in austenite. Using the case depth at 2 h and 30 % sea shell addition, the corresponding diffusivity value was $1.46 \times 10^{-6} \text{ cm}^2/\text{sec}$, which compares with those reported by Okongwu and Paranthaman⁸⁾ and Reed-Hill⁹⁾ as 1.7×10^{-6} and $3.6 \times 10^{-6} \text{ cm}^2/\text{sec}$, respectively. The value reported by Okongwu and co-worker was based on the use of energizers.

4.5. Comparison of Sea Shell with Other Energizers

The effective case depth obtained using other energizers is given in **Table 8** for 2 h carburization.

The table above indicates that BaCO₃ is the best energizer, followed by sea shell which is 82.5 % as efficient as BaCO₃. It is also 134.7 % as effective as lime stone (CaCO₃).

4.6 Comparison of Sea Shell with Gas Carburization

Gaseous carburizing is now the main process of carburizing in mass production while solid carburizing is economical in small scale production. It was found necessary to compare the performance of sea shell (solid carburizer) with gas carburizer. Gaseous carburization is achieved by the decomposition of carbon monoxide and various hydrocarbons to produce atomic carbon as shown^{2,10)}

The atomic carbon (C⁰) is absorbed at the γ -Fe surface to produce hardened case, γ -Fe(C).

Figure 3 presents the case depths and carburizing times at various carburizing temperatures. According to Gulyeav,²⁾ gas carburization was carried out at 930, 970, 1000 and 1050°C and the results displayed in the above figure. Sea shell, solid carburization, was carried out at 950°C and the result is also shown in the figure. The solid carburization at 950°C effectively co-incides with gas carburization at 1050°C. Extrapolation of gas carburization at 950°C, based on Gulyeav's data, is shown as 'dash' line in Fig. 3.

It can be seen from the graph that the shape of the curve for both the sea shell (solid carburizer) and gas carburizer seems to be the same. This could imply similar

Fig. 3. Comparison of sea shell with gas carburization.
(Source: A. Gulyeav²⁾)

phenomenon (mechanism) in the carburization process. Compared with the dashed line, the sea shell showed higher efficiency at the various carburizing times. This means that the sea shell at 950°C is as efficient as gas carburization at 1050°C. There is therefore a significant increase in the kinetics and energy savings using sea shell. Kinetics of sea shell carburization and its implications on industrial utilization is the subject of a paper currently being processed by the authors. The effect of sample size and shape on the efficiency of sea shell carburizing is considered in this paper.

5. Conclusions

The suitability of sea shell and coconut shell as substitute energizers in pack carburization has been examined and the following conclusions made:

- (1) The addition of sea shell to charcoal can produce a significant increase in the carburization rate of mild steel.
- (2) Carburizing compound made up of 70 % charcoal and 30 % sea shell will produce an optimal carburizing effect at all temperatures and holding time.
- (3) Effective average case depth of 1.45, 1.95, 2.60 and 2.80 mm were observed at 2, 4, 6 and 8 h of carburizing with the optimal mixture at 950°C.
- (4) Coconut shell can not be effectively used as energizer at carburizing temperatures (900–950°C) since it decomposes to produce $\text{C} + \text{H}_2\text{O}$.
- (5) Severe scaling problem occurred with coconut shell reaction thus further preventing its use in carburization.
- (6) Sea shell compares favourably with BaCO₃ as energizer, giving a relative efficiency of 82.5 %.
- (7) Sea shell is recommended as a substitute for BaCO₃, considering its ready availability, cost and chemical efficacy.
- (8) Carburization with sea shell as energizer has higher efficiency than gas carburization at the same

temperature and holding times.

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