TABLE IV

Hydrogenation of Methyl Linoleate with Different Rh Complexes at 100 C and 1 atm Pressure (0.4 mole % Rh)

Catalyst	Time (min)	Composition (Rel. %)[a]					T.N. (min^{-1})
		Lo	CD	M	S	S_{Lo}	
$RhCl(CO)(Ph_3P)_2$	320	37.7	5.2	42.8	14.1	2.0	0.57
$[RhNBD(diphos)]+PF_6^-$	200	32.2	4.2	54.7	8.9	4.4	0.79
$RhCl(Ph_3P)_3$	47	8.3	15.6	54.8	21.3	4.5	5.18

[a]Lo = methyl linoleate, CD = conjugated dienes, M = monoenes, S = methyl stearate.

formed either from monoene (k_M 0.29) or directly by double reduction from linoleate (k'_{Lo} 0.05). The 1,2-addition route (k_{Lo} 1.0) producing *cis* monoenes is more than twice as important as the 1,4-addition route via conjugated diene intermediates (k''_{Lo} 0.45). This pathway may explain the formation of low *trans*-unsaturation in a similar system (11). The accumulation of conjugated dienes is significant (Table IV), however, because further hydrogenation of these intermediates is slow compared to the direct reduction of methyl linoleate.

Although the complexes $RhCl(CO)(Ph_3P)_2$ and $[Rh(NBD)(diphos)]^+PF_6^-$ were completely inactive in the hydrogenation of methyl sorbate (Table II), they both catalyzed the hydrogenation of methyl linoleate (Table IV). The turnover numbers for these two complexes were, however, rather low compared to that of the Wilkinson's catalyst. With all these complexes, the accumulation of conjugated dienes was rather high and the linoleate selectivity rather low. Apparently the complex formation between these catalysts and the conjugated triene system of methyl sorbate is much stronger than that with the conjugated dienes formed with methyl linoleate. In methyl sorbate, such complex formation causes complete inactivation of the catalyst. In methyl linoleate, this complex formation results in a slower reduction (k_{CD} 0.55) than that of methyl linoleate (k_{Lo} 1.0) (Fig. 5). The linoleate selectivity values obtained in this study in the absence of solvent are significantly lower than those reported previously in the presence of polar solvents (Table I). Therefore, catalyst solvation may play a key part in the linoleate selectivity of Rh complexes.

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Sunflower Oil Diesel Fuel: Lubrication System Contamination

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ABSTRACT

Diesel lubrication oil contaminated with sunflower oil fuel was exposed to conditions simulating an engine crankcase environment to quantify and elucidate the mechanisms of loss of alkalinity and oil mixture thickening. Oxygen was found to be a dominant factor in both phenomena as was the presence of metallic copper catalyst. Triglyceride polymerization causing oil thickening does not appear causally related to alkalinity loss, but rather seems governed by a separate free radical mechanism.

INTRODUCTION

In recent years the escalating price of diesel fuel and the uncertainty of its availability have spurred research to develop alternate fuelstocks. Seed oils such as sunflower oil show promise as substitute diesel fuels and ultimately may prove acceptable, but problems of oilseed fuel contamination of engine lubrication oil must be overcome. Severe lubrication oil thickening and loss of alkalinity are encountered commonly when plant oils are substituted directly for standard diesel fuel in extended engine testing (1,2).

Thickening of lubrication oil contaminated with oilseed fuel probably is due to addition polymerization at points of unsaturation in the plant oil. As with drying oils, this polymerization might be expected to be accelerated by the presence of oxygen and certain metals (3). Such results, along with a strong relationship between the extent of plant

oil unsaturation and the severity of lubrication oil thickening, have been reported (4,5).

Loss of lubrication oil alkalinity leads to corrosion and increased wear of diesel engine parts. Alkalinity loss can be caused by oxidation of lubrication system components to acids. Siekmann et al. (2) report a sharp loss of alkalinity in lube oil containing transesterified derivatives of soybean oil under simulated engine operating conditions. Again, the presence of unsaturation in the plant oil contaminant probably accelerates production of acidic species which consume the buffering power of lube oil additives.

Most research to date on the problem of plant oil contamination of diesel lubrication oil has involved problem definition in extended engine testing. High experimental costs are incurred in the destructive evaluation of new engine components, and interpretation of results is often complicated by difficulties with experimental control and repeatability. For these reasons, research involving fundamentals of the problem of lubrication oil contamination is best conducted in laboratory simulations of the diesel crankcase environment.

The objective of the present work is to quantify the thickening and alkalinity losses of lubricating oil contaminated with sunflower oil fuel. The impacts of oxygen and metallic copper catalyst on the rise of viscosity and decline of alkaline reserve are sought, and the work attempts to clarify the mechanism of polymerization and its relation to alkalinity loss.

EXPERIMENTAL

Materials

Sunflower oil used in this study was edible grade purchased from Agricom of Berkeley, California. Diesel lubrication oil was Amoco Super HD II Low Ash MIL-L-2104C API CD SAE 30. Amoco 9231, an overbased calcium phenate formulation, was obtained from Amoco Petroleum Additives Corporation, and Lupersol 130, a commercial organic peroxide, was obtained from Lucidol Pennwalt of Buffalo, New York. All other chemicals used were reagent grade.

Treatment of Sample Oil Mixtures

Lubrication oil diluted with sunflower oil was exposed to elevated temperature and catalytic oxidation in an apparatus similar to that described by Bauer et al. (4). Oil samples of 50 ml were placed in 2.5 cm x 20 cm Pyrex test tubes and immersed in a heated oil bath controlled to maintain oil sample temperatures at ±0.05 C. Sample temperatures were measured by chromel-alumel thermocouples immersed in blank cells containing only lubricant. Preheated oxygen or nitrogen was percolated through samples by 7 mm fritted glass bubblers positioned at the bottom of test tubes. Gas flow rates were measured by a Varian Aerograph soap film meter. Copper catalyst, where used, was presented as rectangular wire wrapped around the glass frit. Wire cross sections measured nominally 0.3 mm x 0.07 mm with wire length used to vary catalyst quantity. Copper wire was sanded and cleaned with heptane and acetone prior to use.

A standard set of exposure conditions was utilized for sample oil mixtures, with individual conditions then varied as desired to test for sensitivity. Standard oil bath temperature was 150 C, oxygen flow was fixed at 2000 ml/hr, and 20 cm of copper wire was wrapped around the fritted bubbler for the reference case.

Viscosity Measurement

Viscosities of degraded oil mixtures were measured using calibrated Cannon-Fenske viscometers with ranges from 50 to 1000 centistokes. Temperature of viscosity measurement was maintained at 40 ± 0.05 C in an agitated water bath. Oil samples were returned to heater test cells following viscosity determination.

Total Base Number Measurement

Alkaline reserve of degraded oil samples was measured as a total base number (TBN) according to ASTM D 2896, "Total Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration" (6). This back-titration method was selected to yield sharp endpoints with degraded oil mixtures. A Beckman Model SS-3 Zeromatic pH meter fitted with Corning Ag/AgCl glass membrane electrodes was used for endpoint detection. Total base number testing was destructive, so make-up material was added to heater test cells from other test tubes being treated identically to minimize any impacts of agitation/mass transfer variations.

RESULTS AND DISCUSSION

Samples of diesel lubrication oil contaminated with sunflower oil were exposed to elevated temperature and catalytic oxidation in the laboratory heater bath, simulating conditions existing in a diesel engine lubrication system. Thermal stability of the paraffinic heater bath oil limited maximum sample temperature to 150 C, but this level was felt to be a reasonable compromise between combustion chamber wall and crankcase reservoir temperatures. Copper catalyst was added to oil mixture test cells, as copper is a common wear metal contaminant in diesel lubrication oil (7) and has demonstrated catalytic activity in drying oil polymerization (3).

The effect of concentration of sunflower oil contamination in lubrication oil on mixture thickening is shown in Figure 1, where kinematic viscosity is plotted against time. Exposure conditions are those given earlier as the reference case. Viscosity rise is clearly a strong function of sunflower oil concentration and hence extent of unsaturation of the oil mixture. A sunflower oil concentration of 5.0% by weight was selected for subsequent experiments, because this level falls within the range observed in actual engine

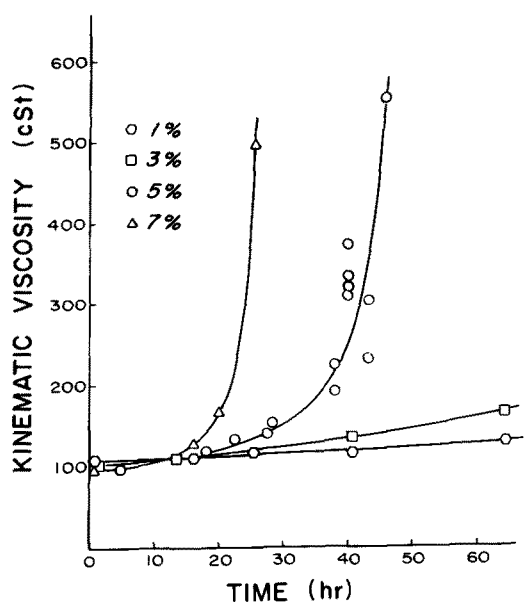


FIG. 1. Oil mixture viscosity vs exposure time at 150 C for various sunflower oil dilution levels.

testing (8) and yields a significant viscosity rise within 40 hr under the conditions of this study.

Figure 2 illustrates the impact of quantity of copper catalyst on oil mixture thickening. In addition to the viscosity rise data of Figure 1 for 5.0% sunflower oil with 20 cm copper wire, data for viscosity against time are given in Figure 2 for 0 and 100 cm of copper wire exposed on the bubbler frit. Viscosity rise, and hence the rate of addition polymerization of the seed oil, is influenced strongly by the presence and quantity of copper wire surface. A wire length of 20 cm was selected for subsequent experiments where copper catalyst was used.

It is interesting to note that polished and solvent cleaned iron wire had no catalytic effect on viscosity rate of rise. When 20 cm lengths of iron were used either alone or with an equal length of copper wire, the viscosity rise responses were essentially unchanged from those given in Figure 2 for copper alone. Iron is the dominant wear metal in used diesel lubrication oil, and work by Bauer et al. (4) using combined copper/iron catalysts indicated a catalytic role for iron in the polymerization of soybean oil at 120 C. It seems likely that the response observed by the Bauer group was due solely to the presence of copper.

Results given in Figures 1 and 2 were obtained at a fixed oxygen flow rate of 2000 ml/hr. The influence on viscosity rate of rise of oxygen presence and flow rate is shown in Figure 3. Once again, the reference curve of Figure 2 for 2000 ml/hr is shown for comparison. Where no oxygen was utilized, nitrogen at 2000 ml/hr was substituted to maintain agitation intensity. Figure 3 shows the presence of oxygen is a primary factor determining the polymerization rate of the sunflower oil contaminant. Doubling the oxygen flow rate from 2000 ml/hr to 4000 ml/hr, however, has only a slight effect on the viscosity rate of rise. The overall polymerization rate appears to be dominated by chemical kinetics and only slightly affected by mass transfer phenomena at the conditions of this study.

Loss of alkalinity of sample oil mixtures is shown in Figure 4, where total base number (TBN) is plotted against exposure time. Reference case conditions were used in Figure 4 with 0 and 20 cm copper wire catalyst. The catalytic effect of copper is pronounced, but oxidation of double bonds proceeds quite rapidly in the absence of copper. The decline of TBN followed a reversed S-curve, with an initial slow reduction followed by a rapid drop and finally a leveling-off interval. The shape of the curves in Figure 4 may be due to the combined effects of chemical and physical system characteristics. Initially, TBN decline is probably slowed by the actions of buffering compounds present in the commercial lubrication oil and natural tocopherol antioxidants in the seed oil. As these buffers and antioxidants are consumed, TBN falls more rapidly until the rate of formation of acidic species begins to slow, probably due to the combined effects of reduced unsaturation and increased viscosity of the oil mixture. When nitrogen was substituted for oxygen at the standard reference conditions, TBN remained essentially unchanged at its initial value over the sample exposure interval.

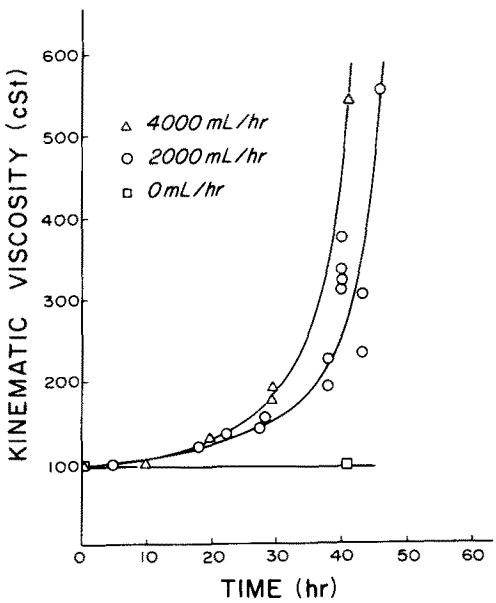


FIG. 3. Oil mixture viscosity vs exposure time at 150 C for various oxygen flow rates.

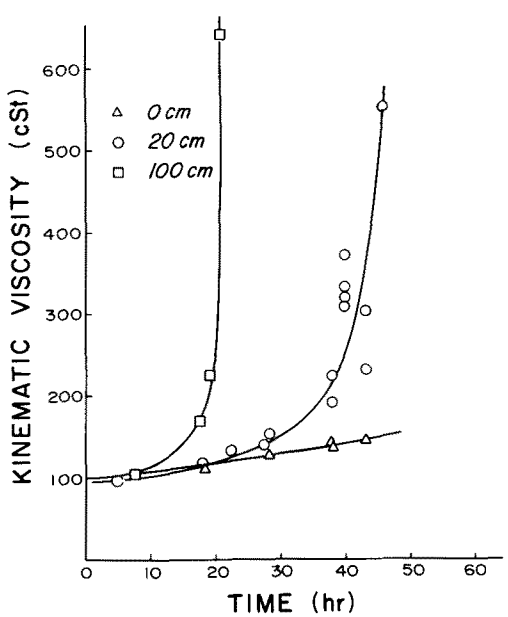


FIG. 2. Oil mixture viscosity vs exposure time at 150 C for various copper catalyst quantities.

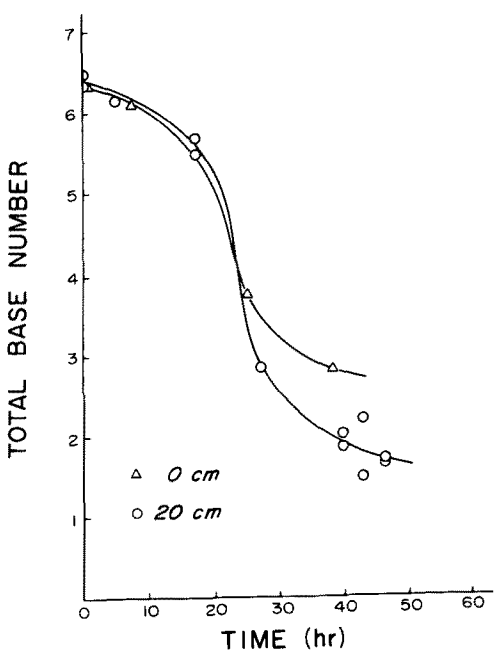
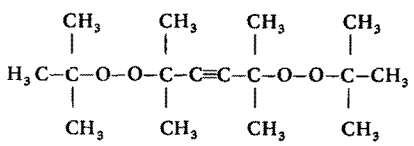


FIG. 4. Total base number vs exposure time at 150 C for 0 and 20 cm copper catalyst wire lengths.

A comparison of Figure 4 with the viscosity rise data for these same reference conditions reveals that TBN falls off abruptly at approximately the same time as the sharp upswing in viscosity commences. Figure 5 gives results of an experiment designed to check whether the addition polymerization of sunflower triglycerides is accelerated by the presence of acidic species in the oil mixture. In this trial, 5.0% sunflower oil sample mixtures were tested at standard reference conditions, but at intervals of about 10 hr additions of between 0.20 and 0.35 gm of Amoco 9231 were made to test cells. This commercial additive, an overbased calcium phenate, is formulated to help maintain TBN in lubrication oil over extended drain-out cycles. The amount of each addition of Amoco 9231 was calculated to reset TBN to at least its initial value of 6.6. Data showing the decline and stepwise resetting of TBN over the course of the experiment are shown across the top of Figure 5. Throughout the run, TBN averaged near 6.0 and at no time fell below 4.0. Viscosity data for this high alkalinity trial also are given in Figure 5, along with the dashed viscosity curve for the reference case with no additions. These two viscosity curves very nearly coincide, apparently establishing that free acidic species have little impact upon the addition polymerization mechanism at the simulated engine conditions of this study.

Having shown that acid catalysis plays little or no role in the addition polymerization, a final experiment was run to confirm the anticipated oxidative free radical mechanism. In this case a trial was conducted at reference conditions with a flow of 2000 ml/hr nitrogen substituted for oxygen, a situation that gave essentially no viscosity rise in Figure 2. However, in this experiment periodic additions of Lupersol 130, a commercial peroxide, were made to sample mixtures. The structure of Lupersol 130 is



Viscosity data for test cells to which 0.1% and 0.5% by weight Lupersol 130 additions were made every 2.5 hr are shown in Figure 6. The dashed line is again the reference case, using oxygen with no peroxide additions. The similar shapes and magnitudes of the curves of Figure 6 indicate that a consistent chain reaction mechanism is at work. The peroxide additive is known to initiate addition chain reactions by first decomposing to free radicals which attack ethylenic carbons. In a similar way oxygen presumably attacks at ethylenic carbons forming quasi-stable hydroperoxides which ultimately decompose to free radicals that propagate the chain reaction polymerization (3). Thus, a free radical mechanism is quite strongly indicated for the conditions of this laboratory simulation. The total base number was unchanged from its initial value for the trial cells of Figure 6 over the course of the experiment.

Results of this study suggest areas for continued research to mitigate the problems of diesel lubrication system contamination by unsaturated plant oil fuels. Antioxidant additives may slow the decline of alkalinity, and free radical inhibitors should reduce the rate of triglyceride polymerization and hence lube oil thickening. Additives that inhibit the catalytic activity of copper wear metal also should be investigated. Obvious problems to be surmounted with any additive approach are excessive volatility and thermal/chemical stability limitations.

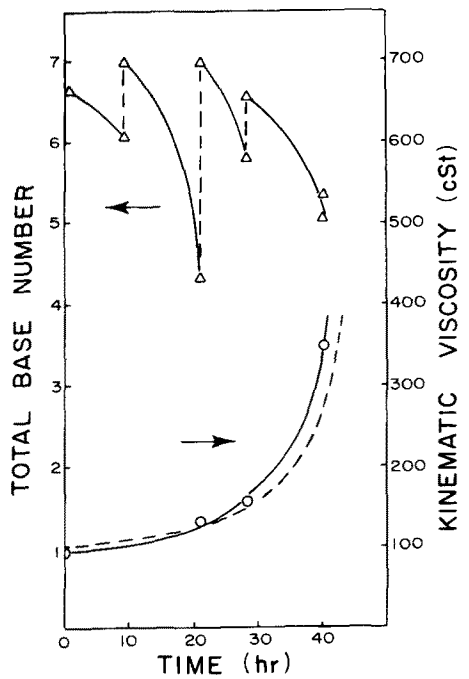


FIG. 5. Oil mixture viscosity vs exposure time at 150 C with TBN maintained using Amoco 9231 additive. Dashed viscosity curve is reference case with no additive.

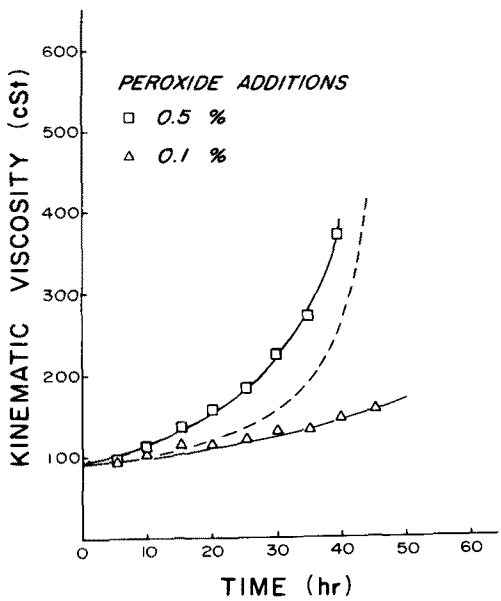


FIG. 6. Oil mixture viscosity vs exposure time at 150 C with peroxide additions. Dashed line is reference case using oxygen flow and no peroxide additive.

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Protease Inhibitors and in vitro Protein Digestibility of Defatted Seed Cakes of Akashmoni and Karanja

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ABSTRACT

Trypsin and chymotrypsin inhibitor activities of defatted seed meals of akashmoni *(Acacia auriculaeformis)* and karanja *(Pongamia glabra)* were studied before and after detoxification. Protease inhibitor activities were significantly higher in the unprocessed seed meals when compared with the processed seed meals. Detoxification also improved the in vitro protein digestibilities of these seed meals significantly. Processed meals of these legume seeds, with lower protease inhibitor activities and higher protein digestibilities, could readily be used as animal feed.

INTRODUCTION

In order to solve shortages and high prices paid for traditional food grains, exploration of non-traditional seeds from different forest plants is imperative. Many unconventional waste seeds can be used profitably for this purpose, and the legume seeds have received much attention as they are good sources of protein and other nutrients. Although the seed proteins are of good quality and contain a number of essential amino acids, the main problem in the nutritional exploitation of these unconventional forest resources is the presence of antinutritional factors (1). Processing or detoxification of these seeds or their meals is necessary prior to their use in animal feed. The nutritive value and protein digestibility of these seeds generally are improved by processing to destroy the antinutritional factors (2). Among these factors, trypsin and chymotrypsin inhibitors have been studied in legume seeds (3,4). The polyphenolic compounds, generally referred to as tannins, also have received much attention (4,5). The presence of free toxic amino acids in legume seeds also should be considered in this context (6), as these antinutritional factors have been reported to reduce the biological value of protein by inhibiting the digestive enzymes; this greatly impairs the nutritive value of the seeds (4-7).

Akashmoni *(Acacia auriculaeformis)* and karanja *(Pongamia glabra)*, members of the family Leguminous, grow largely in India and have been recognized as potential minor non-edible oilseeds (8). India has the potential to produce over 111 thousand tons of karanja seed and 30 thousand tons of akashmoni seed annually, although hardly one-fourth of this capacity is used at present (9). Preliminary analyses (10), refining (11) and nutritional and toxicological evaluations (12) of these seed oils have been reported by this laboratory. Defatted seed meals of akashmoni and karanja have a high protein content, and their amino acid composition suggests they might be used as a valuable supplement in animal feeds (13-15). However, the feeding value of these seed meals is greatly impaired by the presence of antinutritional factors (14,16). In 1984, we devised a simple process for detoxification of karanja seed meal by refluxing the seed meal with 2% HCl. The resultant meal was fed to rats at 30% level of the diet for 30 days without identification of any toxic effects (17). Defatted seed meal of akashmoni also was detoxified by the treatment with lime and subsequent autoclaving; the processed meal, when fed to rats at a 30% level in the diet for 4 weeks, did not reveal any abnormality in growth or in blood or liver biochemical or histopathological characteristics (18). However, additional studies are needed to investigate the performance of these defatted seed meals prior to and after detoxification before they can be recommended as safe for livestock consumption. In this paper, the levels of protease inhibitors and results of in vitro protein digestibility of defatted seed meals of akashmoni and karanja before and after detoxification are reported.

MATERIALS AND METHODS

Materials

Seeds of akashmoni *(Acacia auriculaeformis)* and karanja *(Pongamia glabra)* were collected from the local forests of Burdwan, dried and defatted in a soxhlet distillation apparatus using hexane. The defatted meals were air dried to remove the traces of the solvent and stored at a low temperature until use. Trypsin (E.C. 3.4.21.4, 199 μ/mg) and chymotrypsin (E.C. 3.4.21.1, 61 μ/mg) (Worthington Biochemical Corporation, New Jersey), pepsin, pancreatin and casein (Sigma Chemical Co., St. Louis, Missouri) were used. Other chemicals and solvents used in this study were of AR grade.

Detoxification Process

For the detoxification of akashmoni seed meal, 500 g of the defatted seed meal was mixed thoroughly with 30 g of lime and subsequently autoclaved at 110 C for 8 min, then dried, cooled and stored until use. The methodology was

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