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# Determination of Residual Solvents in Solvent Extracted Meals[1]

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A REVIEW OF THE literature revealed that only a few methods have been developed for the estimation of residual solvents in extracted materials. A modified Pensky-Martens closed-cup flash tester (1) has been used for meal samples. A copper cup flash tester with concentric rings as heating surfaces is claimed (2) to detect solvent residues as low as 0.03%. The lowest flash temp is related to the solvent percentage in the meal. However, while testing this apparatus we found that, at the lower solvent levels (0.03–0.06%), it was difficult to detect "pop" noises or flashes when a test flame was applied at the appropriate temperature.

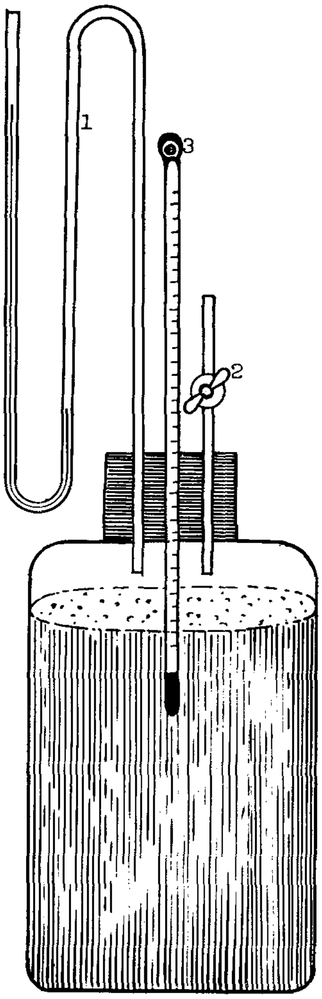

FIG. 1. Apparatus for measurement of solvent residues.

In the course of our work on the solvent extraction of edible quality meals, it became necessary to have a quick method to determine the residual solvent in the extracted meals. A method which we found to be useful is based on vapor pressure of the solvent:

The apparatus consists of a glass bottle which can hold about 300 g meal (Fig. 1), with a tight-fitting rubber stopper carrying a capillary water manometer with scale, a stopcock, and a thermometer.

Meal samples of known solvent content were prepared by a method similar to that of Gastrock et al. (2). The peanut meal used contained 1.5% residual oil and 6% $H_2O$. About 100 g of solvent-free meal were placed in the bottle and the required amount of solvent hexane or heptane added by pipette. The rest of the meal was then quickly added and the stopper fitted tightly. The stopcock, which was open in the beginning, was now closed. After allowing 1 hr for equilibration at the room temp, the pressure recorded by the manometer was noted.

The pressures recorded by the manometer for various hexane and heptane percentages in the meal are shown in Figure 2. The lowest hexane percentage which gave measurable pressure was 0.04%. Gas-

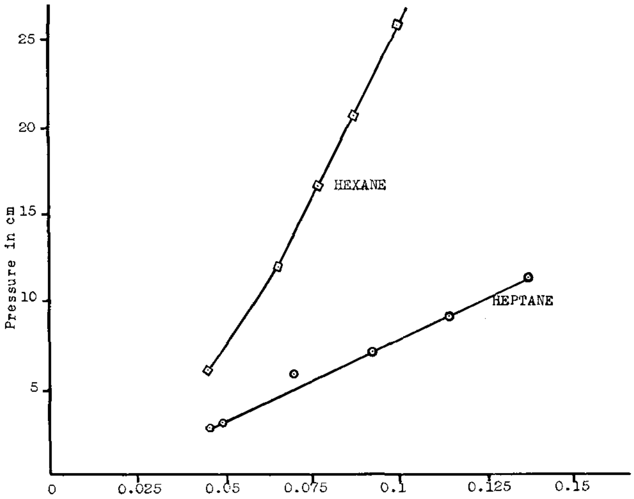

FIG. 2. Per cent solvent in meal.

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[1] Supported in part by P.L. 480, U. S. Public Health Service.

trock et al. (2) and Sikes (1) also could not get positive results by their methods below this level. Even in the closed can test (2), where as much as 1500 g meal were used, no flashes were obtained below 0.04% hexane.

If the apparatus is air tight and the fluctuations in room temp are ± 0.5C, the results are reproducible. Calibration curves will have to be drawn for each solvent at the prevailing room temp for purposes of comparison and quantitative determination. The method seems to have sufficient merit to be considered for plant control purposes.

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# Raney Nickel Catalyst of Improved Stability and Reactivity in the Hydrogenation of Triglycerides[1]

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## Abstract

The degree of activity of Raney nickel catalysts in the hydrogenation of triglycerides has been found to vary considerably with and to depend upon unknown factors in the original alloy. Highly active preparations of Raney nickel rapidly lost their activity when stored in absolute ethanol due to the formation of acetaldehyde. Loss of activity was associated with the amount of residual aluminum in the catalyst. The nickel was found to dissolve to some extent in the acetaldehyde-ethanol solution. Catalysts deactivated by acetaldehyde could be reactivated to a greater degree of activity than that possessed originally by treating with acetic acid. The activity of the original Raney nickel catalyst was preserved to a greater extent by storage in dioxane instead of ethanol.

## Introduction

IN THE COURSE of an investigation directed toward reducing the isomerization of unsaturated fatty acid groups during the hydrogenation of vegetable oils, it became evident that low-temp hydrogenation (below 100C) offered the most promise of attaining the desired objective. Since the nickel catalysts usually employed in the commercial hydrogenation of vegetable oils are not active below 100C, Raney nickel catalysts (2,3), which are prepared from a nickel-aluminum alloy and which are active below 100C, were selected. Most of the investigations were conducted with a specially-prepared Raney nickel designated by the developers as W-5 (2). It reportedly is a more active form than that obtained in the ordinary preparation. However, a W-5 catalyst loses its high activity after about a week's storage in absolute ethanol.

It was discovered that the rapid loss in activity of a W-5 type catalyst during storage in ethanol is caused by the formation of acetaldehyde. The substitution of dioxane for ethanol as the storage medium greatly prolonged the active life of the catalyst. Attempts to reactivate the acetaldehyde "poisoned" catalyst resulted in the development of a method of regenerating the catalyst in a form more active and stable than that originally present. This paper is a report of the details of the work on improving the stability and reactivity of Raney nickel catalyst.

## Experimental

Three different lots of Raney alloy from two commercial sources were used. All of the alloys were of the same general composition. Semi-quantitative spectrophotometric analyses indicated that all contained small amounts of copper, iron, cobalt, and silicon; each particular trace metal was found to be present at ca. the same level of concn in all alloys.

The alloys were activated by a low-temp procedure based on that of Adkins and Billica (2). Sixty g of the alloy was added in one-half hour to a solution of 80 g sodium hydroxide in 300 ml water at a temp of 10–20C. Digestion was continued for 1 hr at a temp below 50C. The digested alloy was washed 5 times with approximately 500 ml water each time, the wash water being removed by decantation. The catalyst was then transferred to a medium-grade, fritted-glass funnel (350-ml capacity) and washed continuously by filtering 12 l water through it. After the water washing the catalyst was washed successively with 450 ml portions 95% ethanol and absolute ethanol. Each portion was divided into at least three smaller ones, and the catalyst was filtered practically to dryness between each addition. A dioxane wash, when used, immediately followed and was performed in the same manner as the alcohol washes. The catalyst was stored in the material last used for washing it. Catalyst prepared by this method will be referred to as W-5 type or low-temp digestion catalyst throughout this report.

The acetaldehyde, acetic acid, and ethanol were of the purest grades available. In all treatments, the quantities of catalyst and treating solution were found not to be critical; it was only necessary to have enough solution to cover the catalyst. Usually 5–10 g catalyst

TABLE I
Composition of Nickel-Aluminum Alloys

| Alloy | Sieve analyses | | | | Chemical composition | |
|---|---|---|---|---|---|---|
| | on 140 % | on 200 % | on 325 % | through 325 % | Al % | Ni % |
| 1 | 0.2 | 5.9 | 25.6 | 68.2 | 45.4 | 50.6 |
| 2 | 0.3 | 9.0 | 22.9 | 67.8 | 47.6 | 49.4 |
| 3 | 0.0 | 2.0 | 15.5 | 82.5 | 45.9 | 51.0 |

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