

# Composition and Oil-Retaining Capacity of Jet-Cooked Starch-Oil Composites

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## ABSTRACT

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Jet-cooked starch-oil composites were evaluated to determine whether the cooking procedure resulted in alteration of the chemical composition of either the starch or oil. Although these composites, both in dry form and in aqueous solution, were highly resistant to separation of starch and oil, there was no evidence of covalent bonding of the components, and composition of the starch moiety was unchanged. Extraction of oil from dried composites with a variety of organic solvents was not effective for complete recovery of oil; an amount of oil representing approximately

5% of the starting weight of the composite could be recovered only after hydrolytic degradation of the starch. Extraction of oil from aqueous solutions of composites was also inefficient for complete oil recovery. The extent of extraction varied with concentration of both starch and oil. Typically, extraction repeated eight times with hexane recovered less than 80% of the oil from solutions with starch concentrations above 0.6%.

Researchers at NCAUR (Eskins and Fanta 1994, Fanta and Eskins, *in press*) have recently reported a process for steam jet-cooking of mixtures of starches and lipids to produce highly stable composites resistant to separation of the hydrophilic and hydrophobic components. In this process, the combination of high temperature, pressure, and the mixing action during passage of sample through a small orifice causes complete gelatinization and solubilization of the starch and intimate mixing of the starch with the lipid. These composites are water dispersible over a wide range of dilution, from soft gels to dilute solutions/suspensions, with no separation of phases, and additional lipid materials can be introduced to the composites results without separation. The composites can be dried to a free-flowing powder and reconstituted without significant alteration of their solubility characteristics. These products have substantial potential for use in low-fat food preparations.

The wide range of concentrations over which these composites are stable is only partially dependent on viscosity. This stability is an important property in establishing the potential usefulness of these composites in low-fat food products, in which texture, mouthfeel, etc. must be maintained during the shelf life of food products. In this study, we have determined the composition of representative products prepared by this procedure and quantitatively evaluated their resistance to separation of the hydrophilic and hydrophobic phases at varying solution concentrations. The study has enabled us to verify the reproducibility of the preparation method and to develop a quantitative basis for describing the solution stability of these composites. This information is necessary both for evaluating commercial usefulness of starch-oil composites and as a first step toward determining the nature of the forces and interactions responsible for their unusual stability.

## MATERIALS AND METHODS

### Production of Composite

Normal, waxy, or amylomaize starch was mixed with water to a solids content of 10 or 20% (dry weight basis). To this slurry,

soybean oil, equivalent to 20 or 40% of the dry starch weight, was added and mixed in a Waring Blendor. The blended mixture was continually stirred to keep starch and oil in suspension in the water. The stirred suspension was pumped through a Penick and Ford jet cooker at a flow rate of 2 L/min, with steam at a line pressure of 65 psi (155°C). Outlet pressure was maintained at 40 psi (140°C). The product was collected in Dewar flasks to maintain temperature and prevent retrogradation, then dried on a drum dryer heated with steam at 30 psi (135°C). The flaky product was ground to a coarse powder in a Retsch mill.

### Compositional Analysis

Starch and amylose content of composites were determined by phenol-sulfuric acid analysis (Dubois et al 1956) and measurement of amylose-iodine complex (Knutson 1986), respectively. A 100-mg sample of composite was dispersed in 10 ml of I<sub>2</sub>- (90%) DMSO, from which aliquots were removed for starch and amylose analysis. Control samples—starch solutions containing proportions of oil equivalent to those in composites—were assayed to verify that the concentrations of oil in the composite samples caused no interference with either assay. Two preparations of each composite (i.e., 20 and 40% added oil) were assayed for starch and amylose content.

Total oil content was determined by hydrolyzing the starch in an aqueous suspension of composite with  $\alpha$ -amylase, then extracting the liberated oil with hexane. A 1-g sample of composite was dispersed in 80 ml of boiling water, then cooled to room temperature to preclude denaturation of enzyme, and reacted with 200 units of porcine pancreas  $\alpha$ -amylase (Sigma Chemical Co.) for 3 hr. Dispersion was transferred to a separatory funnel and extracted with two 20-ml portions of hexane. Hexane was transferred to a tared beaker and evaporated at room temperature; the residue, consisting of extracted oil, was determined gravimetrically. Clarity of the residual oil after evaporation of hexane served as an indicator that residue was free of water. If ambient humidity was high, it was necessary to warm the residual oil slightly to obtain a clear sample. The aqueous solution remaining after hexane extraction of the hydrolyzate was analyzed for carbohydrate content.

### Determination of Oil Retention in Dried Composite

The following solvents and solvent combinations were evaluated to establish the most effective means for extracting oil from dry composites: chloroform, hexane, ethanol, methanol, and 1:2 and 2:1 mixtures of chloroform and methanol. These were tested both by extraction at room temperature and by Soxhlet extraction.

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With Soxhlet extraction, no significant difference in the amount of oil extracted from a given composite was observed with any of the solvents, and room temperature extraction with hexane was equivalent to Soxhlet extraction. For convenience, therefore, room temperature extraction with hexane was used for routine analysis.

For routine analysis, dry samples (1–2 g) were immersed in 100 ml of hexane for 30 min. Hexane was decanted, filtered, and evaporated to dryness and extracted lipid was determined gravimetrically. Each sample was extracted three times; more than 90% of extractable oil was recovered with the first extraction, and recovery with the third extraction was negligible. The extraction procedure was carried out on five separate preparations of composites prepared with normal dent starch and 20 or 40% added oil. Single composites prepared with waxy maize starch and amylo maize starch and 40% added oil were also evaluated.

Samples of composites subjected to dry extraction at room temperature were also hydrolyzed with  $\alpha$ -amylase and the hydrolyzates extracted as described above for whole samples, to compare total oil content from whole and extracted composites. Dry extraction plus hydrolysis of extracted sample was conducted on four separate preparations of 20 and 40% added oil composites.

#### Determination of Extractability of Oil from Aqueous Suspensions

Preliminary experiments were conducted to ascertain the optimum proportions of hexane and aqueous solution for extraction. With water-hexane ratios of 1.5:1 (v/v) or greater, a small volume of emulsion, the amount of which varied with starch concentration and with oil content of the composite, formed at the interface of the aqueous and hexane phases. This ratio of water to hexane was critical; at higher proportions of hexane, no emulsion formed and extractability of oil was diminished. A water-hexane ratio of 2:1 (v/v) was used for routine analysis to ensure optimum extraction throughout the extraction sequence.

Aqueous dispersions were prepared from drum-dried composites at starch concentrations ranging from 0.31 to 5.0%. Control samples were prepared from normal raw starch and from starch that had been jet-cooked with no oil at concentrations of 0.62 and 1.25% starch, with 20 and 40% added oil (based on weight of starch). Starch was mixed with water and an appropriate volume of oil, heated to boiling, and cooled to room temperature.

The standard extraction procedure used was as follows: samples were suspended in 80 ml of water, heated to boiling to disperse the composite, cooled to room temperature, transferred to separatory funnels, shaken with 40 ml of hexane for 1 min, allowed to stand until hexane phase stabilized, and separated, collecting the emulsion with the aqueous phase. Hexane extracts were evaporated to dryness and the amount of extracted oil was determined gravimetrically. Each sample was extracted a total of eight times. All extraction experiments with normal starch composites were run on two different composite samples at each concentration level.

#### Composition

Compositional analysis of composites prepared with normal dent starch and 20 and 40% added oil, and waxy maize starch and amylo maize starch prepared with 40% added oil, are given in Table I. In all samples, a substantial portion of oil was lost during processing in the jet cooker/drum dryer. The amount of loss was constant for samples prepared according to the same formulation and under the same conditions. Specifically, composites prepared with 40% added oil, which would contain 28.6% oil and 71.4% starch on a dry-weight basis if all oil had been incorporated into the composite, were determined by quantitative methods to contain 23–24% oil (standard deviation 0.6) and 80–82% starch. Samples prepared with 20% added oil, for which the final composition of 16.7% oil would be expected, were found to contain 12.8% oil (standard deviation 0.9). Amylose content of samples, as a percent of the starch present, was identical to that of the starting materials, indicating that the cooking/drying procedures had not significantly altered the starch composition.

#### Nature of Oil Retention in Composites

Oil that could be removed by extraction with hexane from the dry product was termed "loosely bound" oil. The remaining oil, which could be recovered only by hydrolysis of the either whole or dry-extracted composite, was termed "tightly bound" oil. The total amount of oil that could be recovered by hydrolysis of whole samples was identical to the amount recovered by dry extraction followed by hydrolysis of extracted samples. Total oil content determined by oil recovery agreed, within experimental error, with the proportion of composite that was not accounted for by carbohydrate analysis (Table I). Content of tightly bound oil from samples prepared with 20 and 40% added oil were similar, in the range of 6–7% (standard deviation 1.7) of total sample weight for composites prepared with normal dent starch, regardless of the amount of oil present in the mixture before jet cooking. The amount of tightly bound oil tended to vary with amylose content of the starch used to prepare the composite; e.g., composite prepared with 40% added oil and waxy maize starch contained 4.3% tightly bound oil whereas a composite prepared with amylo maize starch and the same amount of oil contained 8.4% tightly bound oil.

#### Extractability of Oil from Aqueous Suspensions of Composites

Oil was extracted from aqueous suspensions of composites to determine how readily loosely bound oil separated from the starch matrix in an aqueous environment and to establish whether the presence of tightly bound oil persisted, i.e., whether a stable association existed between starch and lipid or whether the presence of tightly bound oil was due only to entrapment of oil in the starch matrix in the solid state.

Oil extractability from composites was markedly different from that of the mixtures of raw or jet cooked starch and oil used as

TABLE I  
Composition of Jet-Cooked Starch-Oil Composites<sup>a</sup>

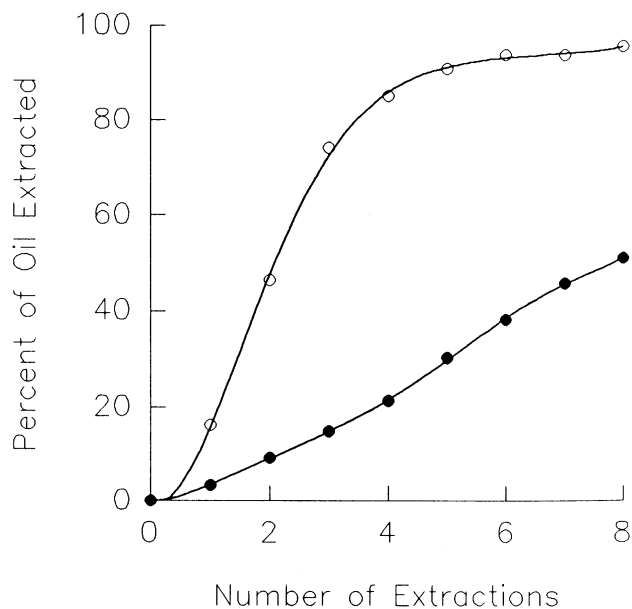
| Starch      | Oil Added      |                           | Carbohydrate<br>in Product, % | Amylose in<br>Starch, % | Recovered Oil, % <sup>b</sup> |               |               |
|-------------|----------------|---------------------------|-------------------------------|-------------------------|-------------------------------|---------------|---------------|
|             | g/100 g Starch | Percent Product<br>Weight |                               |                         | Total                         | Loosely Bound | Tightly Bound |
| Normal      | 20             | 16.7                      | 80.3                          | 21.5                    | 12.8                          | 6.7           | 6.1           |
| Normal      | 40             | 28.6                      | 80.3                          | 21.5                    | 23.9                          | 16.8          | 7.1           |
| Waxy        | 40             | 28.6                      | 80.7                          | 0                       | 23.4                          | 19.1          | 4.3           |
| Amylo maize | 40             | 28.6                      | 82.1                          | 66.8                    | 22.7                          | 14.3          | 8.4           |

<sup>a</sup> Dry-weight basis.

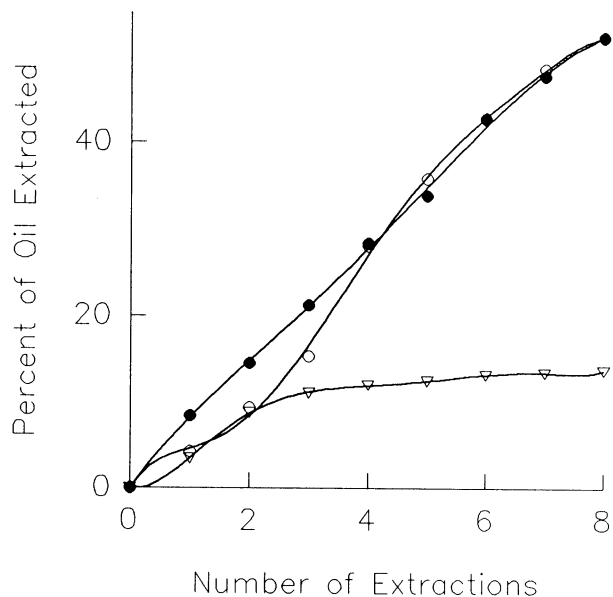
<sup>b</sup> Percent based on weight of product (composite).

control samples. Control samples, when shaken with hexane, initially produced a large volume of emulsion and very small volume of free hexane; the amount of emulsion varied with the amount of oil present, so that each subsequent extraction yielded a larger proportion of hexane and a smaller volume of emulsion, eventually reaching a state at which the emulsion volume was negligible. Composites, on the other hand, produced a relatively small volume of emulsion (approximately 3 g for 20% composite, 6 g for 40% composite), which remained constant from one extraction to the next.

The rate of extraction of composites compared to that of control samples is shown in Figure 1. The percentage of oil extracted is based on the total amount of oil present in the sample as determined by hexane extraction of enzyme-hydrolyzed composite. The difference in these rates vividly demonstrated the oil-retain-



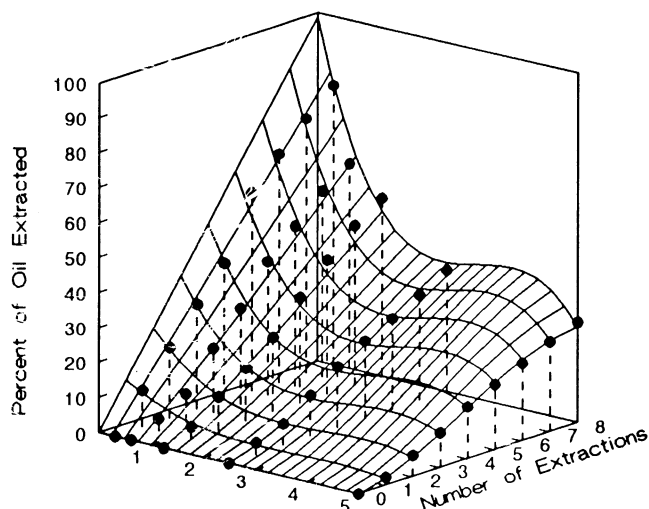
**Fig. 1.** Comparison of extraction rates of oil from a starch-oil composite (●) prepared with 40% added oil and from a mixture of jet-cooked starch and 40% oil (O) heated to boiling and extracted.



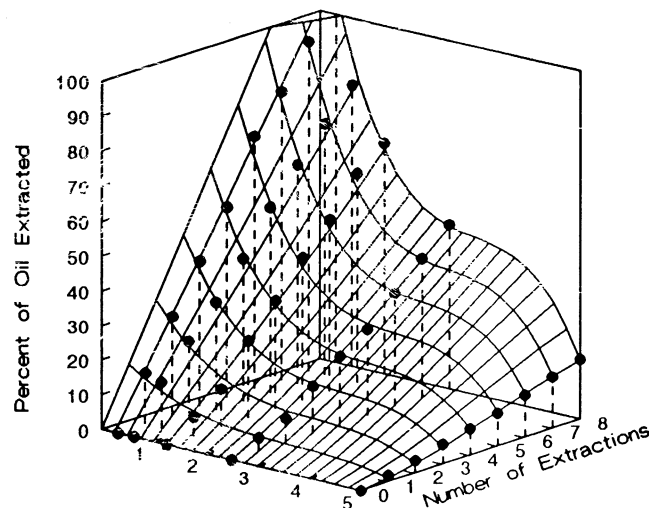
**Fig. 2.** Rate of extraction of oil from 40% added-oil composites prepared with normal (O), waxy (●), and amylo maize (∇) starches.

ing capacity of the jet cooked starch-oil composites. A suspension of composite prepared with 40% added oil at 1.25% starch concentration yielded approximately 50% of its total oil with eight extractions, whereas control samples prepared with either jet-cooked starch (Fig. 1) or raw starch (not shown) yielded more than 90% of their total oil with four to five extractions.

The effect of type of starch on extractability of oil from aqueous suspensions is demonstrated in Figure 2. Composites prepared with normal dent starch or waxy maize starch and 40% added oil at 1.25% starch concentration were very similar. The equivalent composite prepared with amylo maize starch behaved much differently, releasing only 11% of its oil after three extractions and 14% after eight extractions. Further examination of the suspension of the high-amylose composite revealed a high content of starch that swelled but did not redissolve in boiling water. This fraction could be separated from the soluble portion by centrifugation and was resistant to enzyme hydrolysis. When this fraction was redried and finely ground, additional oil could be extracted from the dried sample.



**Fig. 3.** Extraction of oil from 40% added-oil composites at varying starch concentration. X-axis, starch concentration; y-axis, number of extractions; z-axis, percent of oil extracted.



**Fig. 4.** Extraction of oil from 20% added-oil composites at varying starch concentration. X-axis, starch concentration; y-axis, number of extractions; z-axis, percent of oil extracted.

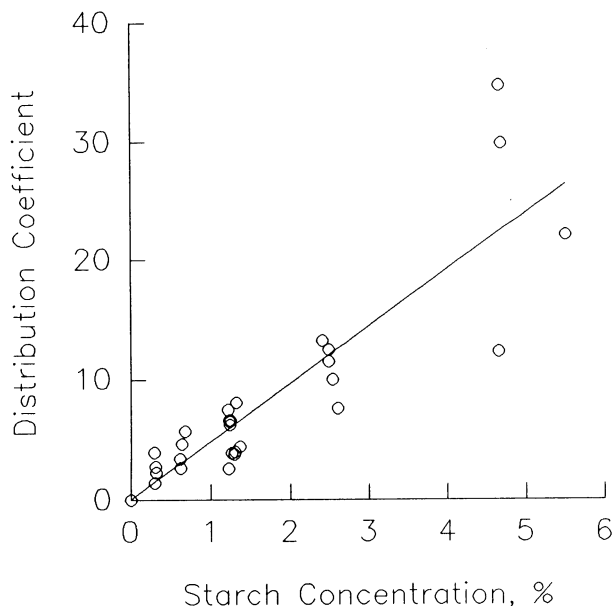


Fig. 5. Effect of starch concentration on water/hexane distribution coefficient of aqueous suspensions of starch-oil composites.

The effect of starch concentration on oil extractability was evaluated on solutions of composites containing 20 and 40% added oil, at starch concentrations from 0.31 to 5%. Data from eight extractions for each of five concentrations of each composite were fitted to three-dimensional plots using a third-order polynomial expression. A correlation coefficient greater than 0.98 was obtained for composites prepared with normal starch and 20 or 40% added oil (Figs. 3 and 4). Rate of extraction of oil decreased with increasing starch concentration. At the lowest starch concentration used (0.31%), essentially all oil could be removed with eight extractions from a 20% composite, and 80% of total oil from a 40% composite.

It is important to note that none of the oil in these composites could be considered "unbound" oil comparable to that mixed into control samples, i.e., no measurable amount of oil separated on standing or was rapidly removed by hexane extractions. By the same token, there appeared to be no demarcation between loosely bound and tightly bound oil in aqueous suspension, and it seems likely that all the oil would eventually be extracted from any given sample by a sufficient number of extractions, as evidenced

by the near-quantitative recovery obtained from the 20% added oil composite extracted at 0.31% starch concentration (Fig. 4). Thus, any designation of tightly vs. loosely bound oil in these composites is only appropriate when speaking of dry materials.

Distribution coefficients,  $K_{(\text{aqueous/hexane})}$ , were calculated from extraction data of composites with varying oil contents and varying concentrations of normal corn starch. Plotting  $K$  values for six different composites containing 20–40% added oil indicated relatively little variation due to a difference in oil content, but a significant effect of starch concentration, as was expected from extraction patterns shown in Figures 3 and 4. Linear regression analysis of  $K$  vs. starch concentration, shown in Figure 5, gave a slope of 4.8, with a standard error of 0.5 and a correlation coefficient of 0.8. That is, the affinity of oil for the starch-water phase relative to the hexane phase increased by a factor of 4.8 for each increase of 1% in starch concentration.

## CONCLUSIONS

Jet cooking of mixtures of starch and oil produced composites in which oil was held tenaciously in both the dry state and in aqueous suspension. Quantitative analysis indicated no change in the starch composition, and there was no evidence of chemical reaction between the starch and the oil. The stability of these composites appears to be due to the complete solubilization of starch and elimination of secondary starch structures at the high temperatures used in the jet-cooking process. Because of this lack of structure in the starch molecules, intimate mixing of starch and oil can occur during cooking, allowing contact between the oil and the lipophilic regions (i.e., interior regions of helices) of the starch molecules. These conditions result in stable composites that have numerous potential uses and should be especially useful for preparation of food products with reduced fat content. Preparation of such products is currently under investigation.

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