

explanation of all of the reactions occurring as peroxides form and decompose.

Summary

1. A study of reaction time and the effect of oxygen on determination of peroxide by the acetic acid-potassium iodide method shows that a one-hour reaction time in the absence of oxygen is necessary, especially on samples of high peroxide.

2. The peroxide-formation curves at 100°, 75°, 55°, 35°, and 15° show a progressive increase in maximum peroxide value reached as the temperature is lowered to 35°. At 15°, the maximum is the same as at 35°; this value is over 30 percent of what it would be if all the double bonds were converted to peroxide.

3. The agreement between actual peroxide and "theoretical peroxide" calculated from decrease in iodine number extends to higher peroxide values as the temperature is decreased.

4. The rate of decomposition or disappearance of peroxide at 100°, 75°, 55°, and 35° agrees best with that of a bimolecular reaction, but definite exceptions exist.

5. The speed of decomposition of peroxide becomes progressively greater as the degree of oxidation is increased.

6. The changes in unsaturation, OH number, and acid number are small compared to the decrease in peroxide value as the peroxide decomposes. The formation of volatile and inflammable products was qualitatively observed in the decomposition of highly oxidized esters.

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Determining Recoverable Fat Losses In Plant Waste Effluents

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Introduction

This problem has always been a serious interest to all primary producers of fats and oils and to those engaged in processing such material into products for commerce. The required operations are of such nature that losses are bound to occur in many ways if due care is not taken. It isn't the purpose of this discussion to elaborate on or even attempt to list all the places or manners in which fat and oil can be lost, or vice versa, salvaged in industrial operation. Many of them are better recognized by the readers of this journal than by any other single technical group.

From a number of years active experience in trying to reduce losses of fats down the waste lines in meat packing plants, and to recover what does tend to get away, sufficient problems have presented themselves to give us a fair idea what constitutes adequate recovery and how to recognize it.

Before proceeding, I wish to acknowledge and give credit to the man who outlined, directed and enthused our interest in this work, namely Mr. M. D. Sanders, now serving as a captain in the United States Army.

Losses of fat and oil that are usually considered irretrievable are those that occur when material is hauled to the dump, carried away in water that goes to the sewer, or becomes incorporated in product whose value is not determined by the fat content. Of these, the one about which something can be done is the loss to the sewer beyond the plant area.

Regardless of ceaseless repetition, of the maxim "Save at the source," it still deserves everyone's con-

stant concern. That means to the fullest possible extent, keep the fat from getting started off on water carry. By taking adequate care at this point, recovery facilities can be adequate without being too numerous or too large. If fat or oil gets into water which is flowing to waste, hundred per cent recovery is not possible thereafter, and any recovered fat will be of poorer quality than the original.

Considering that, in spite of all precautions, some fat does get into the waste water flow, some equipment should be provided for its salvage or interception. When we speak of waste water flow, we mean all clean up water, process water, condenser water, etc., which leaves a plant. This means the installation of intermediate catch basins, traps and sumps followed by, or rather, discharging into one or two final settling basins for one last attempt to insure minimum carry away to outgoing sewer lines.

At this point, it may be well to interject the thought that fat and oil salvage from plant effluents is of interest not only directly from a dollar return on product recovery. The indirect advantages also are large. Excessive fat losses may result in blocked sewers, severe interference with sanitary waste treatment facilities and the pollution of streams into which the sewers discharge.

There is only one practical way in which to recover fats and oils from waste flows. That is by adequate detention, or more correctly, flow velocity reduction in some form of tank, basin or flume so that fat can rise to the surface and be skimmed off.

There isn't the time to discuss in detail with you the requirements of basin design to get the best recovery. In brief, the capacity should be such that the calculated velocity of flow through the basin, to handle the average volume, is not over 1 foot per minute. One underflow baffle should be provided just ahead of the inflow lines to reduce the turbulence effect produced by the incoming waste. No other baffles are required except another underflow just ahead of the final outlet weir or line. An excess of baffles only tends to increase the flow through velocity and defeats the primary purpose of a catch basin. Adequate skimming facilities should be provided such as continuous traveling flights, or a skimmer mounted on wheels or a simple movable baffle to collect the floating material without dipping up too much of the water. Also, provision should be made for completely emptying the basin and cleaning out the settled solids. This may be necessary as often as once every day.

There are special aids to increase the recovery efficiency such as passing air from diffuser tubes through the waste as it first enters the catch basin. Air plus small traces of chlorine is sometimes used. These have never proved of sufficient extra benefit to receive marked attention. For wastes exceptionally high in emulsified fats or soluble soaps, acid treatment can increase recovery enough to be of interest. This is something out of the ordinary and not often resorted to.

In leading up to our main discussion, it should be worthwhile to consider just what we have to deal with when considering plant wastes for fat recovery. First, the flow consists of 99 to 99.9% water containing a varying number of parts per million of soluble organic and inorganic material. The concentration of either of these may vary from a mere trace to considerable quantities depending on the type of operations contributing the waste flows. Of course, there is no recovery of the soluble materials and their importance is due only to their effect in tending to emulsify the fats. The important fraction in the waste consists of insoluble material which may vary in size from minute colloidal particles to gross chunks. It will consist of sand, grit, cinders, meats, grain and hay plus fatty material as discrete particles or droplets of which some will be thoroughly emulsified. The fats may be free or be absorbed on the non-fat material. When this composite mixture is flowing rapidly, sufficient turbulence exists to keep everything uniformly distributed throughout any part of a sample section. By reduction of the velocity of flow separation is started due to differences of density of the insoluble particles and the water media. The unemulsified fats rise to the surface rapidly, emulsified fats very slowly if at all, and some of the light non-fat material such as hay and fiber rise, also. The denser non-fat material and some fatty issue will settle to the bottom. The rate of upward or downward movement of a particle with fat absorbed on it depends entirely on density differences. It may rise, remain in suspension or settle. After reasonable detention at a minimum velocity of flow, a partial separation will have resulted. The surface of the settling tank contents will have a layer of high fat content material, called skimmings, the bottom a layer of settled solids, or sludge. The intermediate layer of water will be fairly free of suspended solids, except those with densities close to that

of water, and will carry only thoroughly emulsified fats or insoluble soaps plus soluble soaps in solution. The latter along with other organic material tends to aid in establishing and maintaining the emulsion. The outflow waste water from the basin plus the sludge remaining will contain the unrecoverable fats or fat-bearing material. The floating fraction, skims, contains the recoverable fats which may be almost entirely saved as a low grade grease or oil by rendering or drying the skimmings and then separating by pressing.

Visual observation and guessing are not adequate means of estimating losses from questionable recovery basins or through lines without interception facilities. The standard method has been to install a weir in a flume at the outlet of the basin or in the sewer to measure the flow rate, and, at definite intervals, say every 5, 10, or 15 minutes, to catch a sample at the weir overflow and also to measure at that time the head of water over the weir crest. The weir reading is converted into the proper flow volume by formula and the readings in gallons per minute are averaged. The sample for the analysis may, if really accurate results are desired, be composited on the basis of the flow at the time of catching each individual sample. If such accuracy is not required, the sample for analysis can be made up from a mixture of all individual samples taken. This sample, or the composite, is analyzed for total fat content as outlined by the Standard APHA (1) method. This, in brief, consists of evaporating to dryness a weighed quantity with sufficient acidification to split the soaps present. This last step is sometimes not done. The dry residue is extracted with petroleum ether to get out the fats, oils and fatty acids. The fat concentration is reported in parts per million and from the flow data the total pounds of fat lost can be calculated.

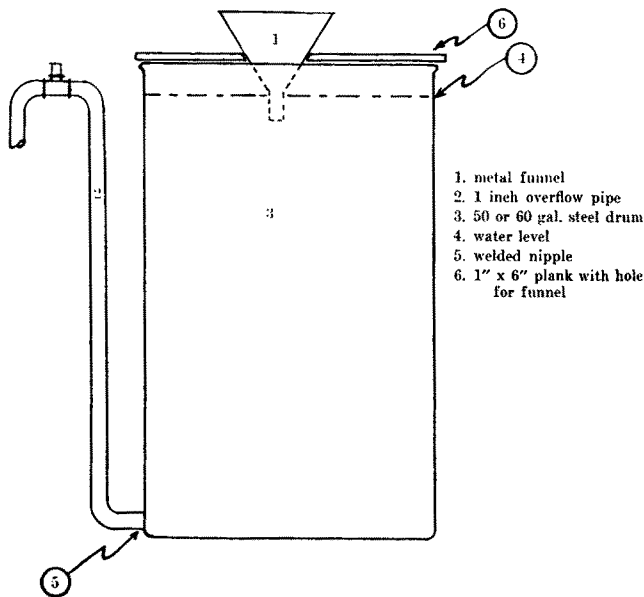
To one who has had more than average interest in improving fat recovery by adequate catch basins, the above described determination for fat loss is very unsatisfactory. In fact, it does not mean much at all for there exists no way of getting out all the fat in the waste flow. It does give an overall loss figure which may have some interest. Obviously the standard method of recovery, namely by settling out at reduced velocity, only gets out one part of the fats and oils. It is only that which floats during quiet flow. In some rare cases, the sludge, after removal, is treated to recover its fat and protein. From all the above considerations, it is obvious that determining the total fat loss in unprotected lines or from ineffective basins doesn't tell the story wanted. In other words, it is not the total fat loss which can be saved. It is fallacious to assume that every pound, based on the total fat loss determination, will be recovered or that any arbitrary standard of performance could be set up for outgoing waste. To do this would require extensive tests covering every field of fat and oil production and processing. To clarify this point of view, what, off hand, would you think should be the attainable minimum total fat content in waste emanating from cattle slaughter operations, cottonseed oil refining, deodorizer hot-well overflow, or glue production operation? You can't very well answer that or determine an arbitrary standard for the minimum content of emulsified fats and oils or the fats absorbed on dense material, since it may vary in one case from a

15 to 50 p.p.m. while in another from 500 to 2,000 p.p.m.

Recognizing this difficulty, and still wanting to provide salvage facilities that will be justified on the basis of product saving our check method on doubtful basins or improperly protected waste lines has been as follows:

As in the total fat loss check method just described, a weir is installed to measure the volume of flow. Then, instead of catching a relatively few and small samples, such as a pint or quart, every 5, 10 or 15 minute interval, a rather large sample is caught every 5 minutes and poured into a 55 gallon steel drum. This drum is provided with an overflow line as illustrated in Figure 1. By catching five one-gallon sam-

SAMPLING BARREL FOR RECOVERABLE FAT



1. metal funnel
2. 1 inch overflow pipe
3. 50 or 60 gal. steel drum
4. water level
5. welded nipple
6. 1" x 6" plank with hole for funnel

To Operate:

1. Barrel is first filled with clean water.
2. Gallon samples, drawn at definite intervals are poured into the funnel.
3. Overflow pipe is adjusted so water will not spill over sides of the barrel.
4. At the end of the test, floating solids are skimmed, weighed, and analysed for fat.

Calculation of Results:

$$\text{Lbs. fat in skimmings} \times \frac{\text{Total volume sampled}}{\text{Volume poured thru funnel}} = \text{lbs. recoverable fat.}$$

ples every five minutes waste is put through the drum at the rate of one gallon per minute. With a 55 gallon

capacity drum, a theoretical detention of approximately 60 minutes is provided with a theoretical flow through velocity which is much less than the usual design calls for, namely, not over 1 foot per minute. This amount of sample and size of test drum was chosen primarily for its convenience to use and its availability. Larger or smaller test units could be used except that too small a unit magnifies any error because of poor final skimming when the sample is taken. At the end of the sampling period, everything floating on the drum is very thoroughly skimmed off, weighed and analyzed for fat. From the total flow data based on weir readings, quantity in gallons of sample put through the drum and weight of fat salvaged a calculation as follows: Lbs. fat in skimmings

$$\times \frac{\text{total volume sampled}}{\text{volume poured through funnel}} = \text{lbs. recoverable fat}$$

gives the pounds lost that can correctly be assumed recoverable by adequate interception facilities. This sort of check is ever so much more practical because it truly gauges the pounds of fat one can figure on saving and thereby one can know how much of an expenditure will be justified in saving it. It removes the guess work, provides the superintendent with the visual proof that recoveries are possible, and establishes a sound approach to fat salvage efforts from industrial waste effluents.

It should be pointed out that some inaccuracy results from a constant rate of sampling rather than composite sampling but this error is not of such magnitude so as to interfere seriously. This does not provide a solution to the problem of economic recovery of non-floating fat. That is a problem to be tackled at the place of actual operations or by segregation of such concentrated wastes for special chemical and/or mechanical treatment.

Sufficient improvements of recovery facilities are required in industrial plants to justify considerable testing by this recoverable fat loss method to establish where settling equipment is best needed or old units should be improved. To accomplish recoveries better than those achieved by settling means, as stated before, requires special treatment and this would be justified only after extensive test work of more complicated nature than just described.

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