Sept. 14, 1948. G. THODOS ET AL 2,449,427

FOAM PREVENTION IN EXTRACTIVE DISTILLATION OF HYDROCARBONS WITH FURFURAL SOLVENT

Filed July 28, 1944 3 Sheets-Sheet 1

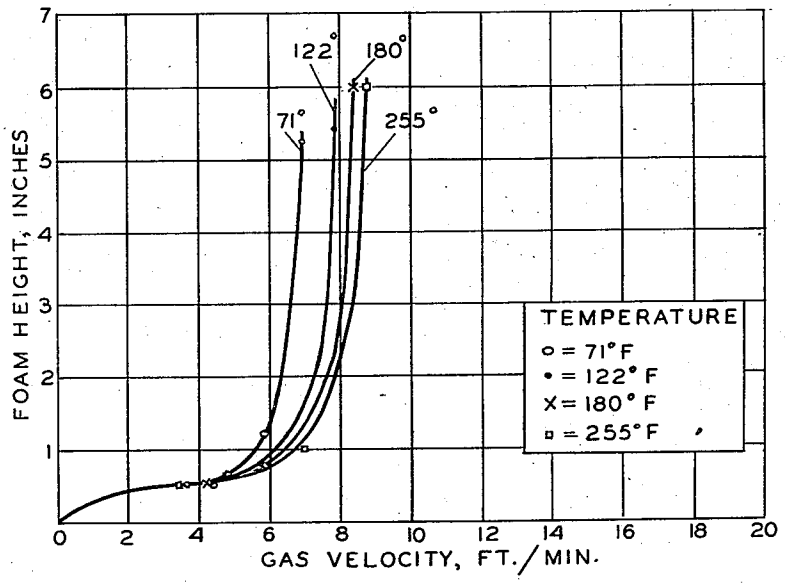



FIG.-1

FOAMY FURFURAL ALONE

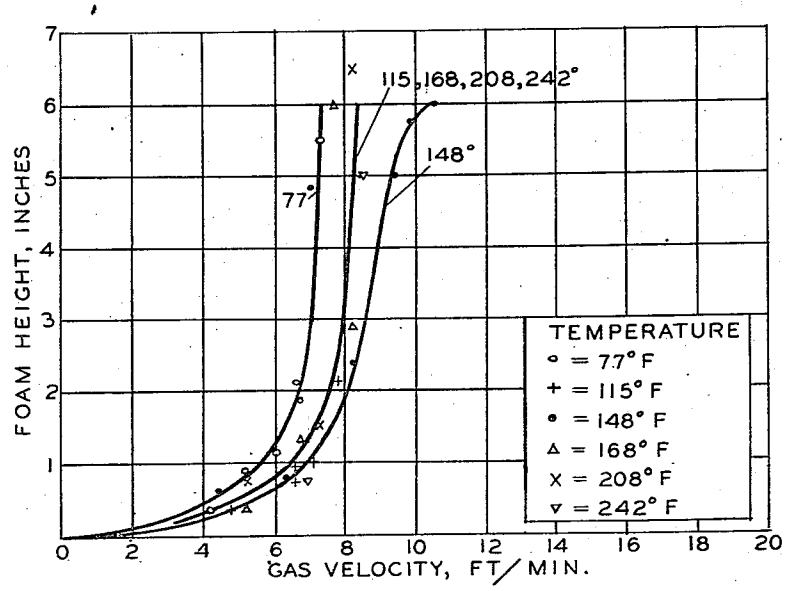



FIG.-2

0.00296 WT. % BEESWAX IN FURFURAL

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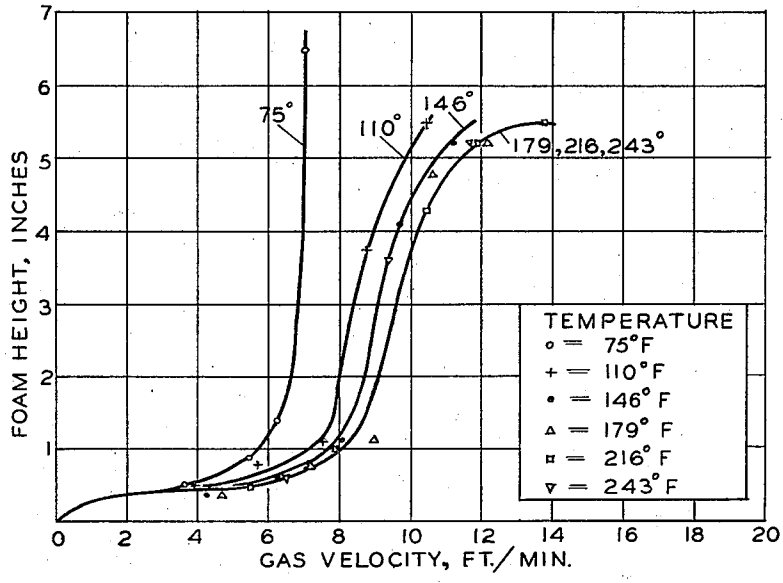



FIG.-3
0.0635 WT. % BEESWAX IN FURFURAL

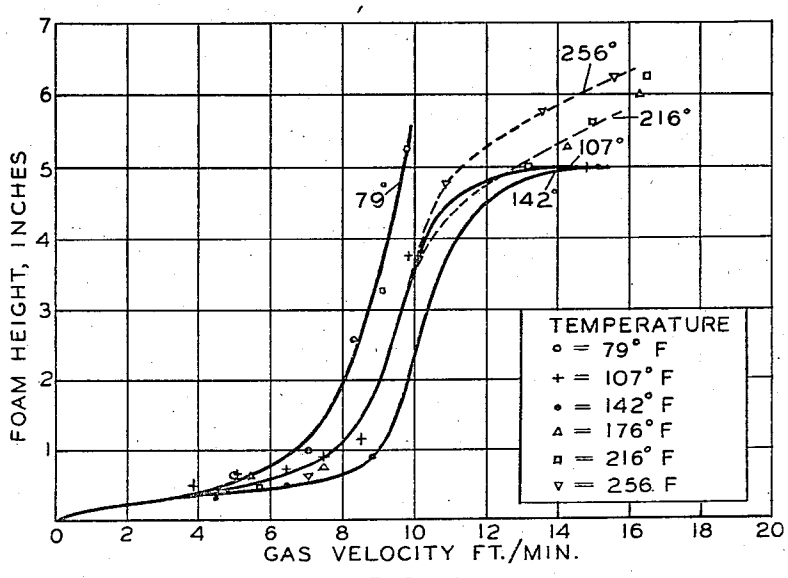



FIG.-4
0.109 WT. % BEESWAX IN FURFURAL

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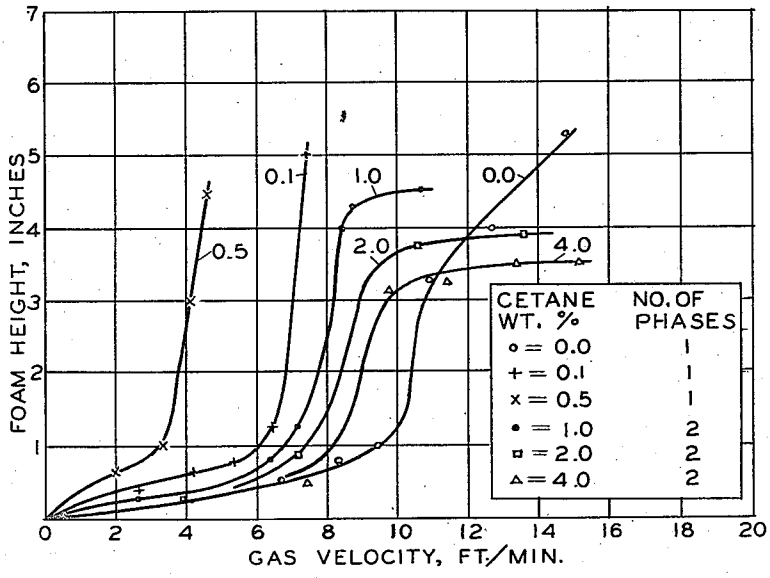



*FIG.-5*
FURFURAL-CETANE SYSTEM AT 80° F

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## FOAM PREVENTION IN EXTRACTIVE DISTILLATION OF HYDROCARBONS WITH FURFURAL SOLVENT

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4 Claims. (Cl. 202—39.5)

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This invention relates to extractive distillation. More particularly it relates to extractive distillation using furfural as the solvent. Still more particularly it relates to the suppression of foaming of the furfural solvent in the extractive distillation of hydrocarbons. Still more particularly it relates to the suppression of foaming of the furfural solvent in the extractive distillation of unsaturated hydrocarbons. Still more particularly it relates to the suppression of foaming in the extractive distillation of butadiene and/or butene from a mixed $C_4$ hydrocarbon stream by means of furfural.

In the extractive distillation of unsaturated hydrocarbons, particularly butadiene and/or butene, from a mixed $C_4$ hydrocarbon stream with furfural as the selective solvent, the furfural gradually accumulates hydrocarbon impurities which bring about foaming difficulties. Foaming of the furfural results in inefficient operation of the extraction and stripping equipment and also results in the carrying over of furfural into the overhead hydrocarbon products of these operations. The foaming occurs both in the extractive distillation column itself and in the stripping column.

While it is not desired to be restricted to any theory, it is believed that the foaming difficulties are caused principally by foreign materials present in the furfural in the system. These foam-producing contaminants may include mineral seal oil, lubricating oils and greases, furfural polymer and polymerization products. It may be that these contaminants increase natural foaming tendencies of the furfural.

The principal object of the present invention is to provide means for suppressing foaming of the furfural used in extractive distillation processes. Another object is to overcome foaming where the furfural solvent becomes contaminated with foam producing substances. Another object is to eliminate foaming in a simple and economical manner. Numerous other objects will hereinafter appear.

In the accompanying drawing Figures 1 to 5 are graphical representations of the foaming tendency at varying temperatures of furfural by itself and furfural to which has been added foam-suppressing agents in accordance with the present invention. Fig. 1 is comparative being based on foamy lean furfural without any foam-suppressant. Figures 2 to 4 show the effect of varying amounts

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of the preferred foam-suppressant, beeswax. Figure 5 shows the effect of cetane.

At this stage in the art, it is not necessary to enter into a detailed discussion of extractive distillation with furfural. It will suffice to state that the extractive distillation system comprises an extractive distillation column into the top of which is introduced the lean furfural which descends countercurrently to the stream being extracted and fractionated. The furfural rich in the desired unsaturated hydrocarbon is withdrawn from the bottom of the extractive distillation column and fed into a stripping column where the unsaturated component is driven off from the furfural. The stripped furfural is then recycled to the extractive distillation column. Such a process is described in detail in the copending applications of Hachmuth, Serial No. 438,844, now Patent No. 2,434,796, dated January 20, 1948, filed April 14, 1942, and Serial No. 482,435, now Patent No. 2,411,785, dated November 26, 1946, filed April 9, 1943.

It has been found that foaming of the furfural in an extractive distillation system can be suppressed by the addition of organic compounds of lesser density than furfural and also possessing limited solubility in furfural provided that such compounds are added to the furfural in excess of their solubility therein. Aliphatic hydrocarbons as well as esters of varying degrees of saturation have been successfully employed as foam-suppressing agents. For example, normal pentane, normal hexane, normal heptane, normal octane, isooctane, kerosene, cetane (normal hexadecane), mineral seal oil, linseed oil, hydrogenated cottonseed oil and butter were found capable of suppressing foaming once their solubility in furfural was exceeded.

Beeswax has been found to be the most successful agent for the suppression of foaming of furfural. The beeswax-furfural system has been extensively studied at different temperatures and concentrations of beeswax. The temperatures were varied from 71 to 255° F. and the beeswax content from 0.00296 to 0.196 weight per cent of beeswax based on the weight of furfural. In all cases no marked decrease in foaming was noticed until the temperature of the system was increased to the melting point of the beeswax. Inasmuch as extractive distillation of unsaturated hydrocar-

bons is commonly carried out at temperatures above the melting point of beeswax, this limitation on operating conditions imposes no disadvantage.

The degree of foaming of lean furfural decreased to a minimum at temperatures around 145° F. apparently the point at which beeswax melts in furfural but failed to maintain this behavior at higher temperatures for concentrations lower than 0.0635 weight per cent of beeswax. For concentrations equal to or exceeding 0.0635 weight per cent and temperatures as high as 255° F., the degree of furfural foaming was found to have decreased abruptly.

The disadvantage of using paraffin hydrocarbons and vegetable oils is that while these materials will suppress foaming at room temperatures once their solubility in furfural has been exceeded, with the same concentrations as were used for the tests conducted at room temperatures these substances did not prove effective in suppressing foaming at elevated temperatures (150° F. and higher) because of their complete solubility in furfural. At these high temperatures excessive amounts of these substances would be required in order to exceed the solubility in the furfural.

It has been found however that the preferred material, beeswax, remains only partially and sparingly soluble in lean furfural at elevated temperatures and at the same time suppresses foaming.

Beeswax added to foamy lean furfural used in the extractive distillation of unsaturated $C_4$ hydrocarbons at room temperature brought about a slight decrease in foaming. Upon increasing the temperature of the system the foaming tendencies of the lean furfural were markedly decreased. Eight different concentrations of beeswax were investigated in order to ascertain the effect of concentration of beeswax upon foaming at different temperatures. A concentration of 0.0635 weight per cent of beeswax was found critical. For all concentrations smaller than this the foaming tendencies decreased up to temperatures as high as 150° F. but above 150° F. the foaming tendencies increased. This is illustrated in Figure 2 of the drawing. Beeswax concentrations equal to or greater than 0.0635 weight per cent were found capable of suppressing the foaming at temperatures as high as 250° F., the foaming results at different temperatures being shown in Figures 3 and 4. The relative magnitude of foam suppression caused by the presence of beeswax in the concentrations and at the temperatures shown in Figures 2, 3 and 4 can be ascertained by comparing these graphs with the graph of foaming tests on the foamy lean furfural in Figure 1.

The curves portrayed in Figures 1 to 5 of the drawing were made by passing butene-2 at various linear gas velocities upwardly through a horizontal, sintered glass plate in the bottom of a bubbler tube and then through a liquid column of the furfural resting on this plate. The static liquid height was 1.50 inches. The gas passing through the interstices of the sintered glass plate was broken up and ascended through the liquid layer in the form of bubbles. The foam height in inches was plotted against linear gas velocity at the cross-sectional area of the bubbler (the area of the porous plate) in feet per minute. This foam height relative to lean furfural was found to be a criterion of the foaming tendency in the extractive distillation column and in the stripping column of the extractive distillation unit. The foaming characteristics of the foamy furfural were found to be nearly the same when normal butane and butene-2 were used.



The furfural used in all of the tests represented by Figures 1 to 5 was foamy lean furfural from the extractive distillation of butene-2 and contained the usual small amount of dissolved water. While Figures 1 to 4 will be substantially explanatory in the light of the foregoing, it may be stated that the effect of the beeswax when added in excess of its solubility at temperatures above its melting point is to cause a flattening of the curve as the linear gas velocity is increased. The point at which this flattening occurs and the extent of the flattening are a direct indication of the foam-suppressing characteristics of the agent in question. The greater this flattening the greater the foam-suppressing action of the beeswax.

Figure 5 portrays the effect of cetane on furfural. It will be noted that when the concentration of the cetane equals or exceeds 1.0 weight per cent based on weight of furfural, at which two phases are present, a very marked flattening of the curve is exhibited.

The present invention is applicable both to anhydrous furfural and furfural containing small amounts of dissolved water. The process of extractively distilling unsaturated $C_4$ hydrocarbons with a solvent of furfural containing small amounts of dissolved water is described and claimed in the copending application of Hachmuth, Serial No. 438,844, referred to above. It has been found by actual tests that water tends to decrease the foaming tendencies of pure furfural, increased water concentrations causing decrease in foaming. However the presence of water in furfural contaminated with foam producing agents tends to increase foaming.

It is noteworthy that while small amounts of mineral seal oil and other paraffins increase the foaming, addition in excess of their solubility in the furfural effects a marked decrease in foaming.

While the invention is particularly applicable where furfural is used as the selective solvent in the extractive distillation of unsaturated hydrocarbons, the carrying out of separations between saturated hydrocarbons, for example between paraffins and naphthenes, or between aromatic and aliphatic or alicyclic hydrocarbons, for example between paraffins or olefins and aromatics or between naphthenes or cyclo-olefins and aromatics is within the scope of the invention.

From the foregoing it will be seen that the present invention presents a number of advantages over the prior art. It enables the suppression of foaming tendencies of the furfural in a simple and economical manner. The foaming tendencies are reduced without interfering with the selectivity of the solvent for the unsaturated hydrocarbon. No substantial disadvantages attend the suppression of foaming in accordance with the present invention.

As used herein, "butene-2" refers to a mixture of the high and low-boiling isomers.

We claim:

1. In the extractive distillation of hydrocarbons with furfural as a solvent wherein the furfural becomes contaminated with foam-producing substances, the improvement which comprises suppressing foaming by admixing with the furfural used as the solvent beeswax in amount which is substantially in excess of its solubility in said furfural.

2. In the extractive distillation of unsaturated hydrocarbons with furfural as a solvnt wherein

the furfural becomes contaminated with foam-producing substances, the improvement which comprises suppressing foaming by admixing with the furfural used as the solvent beeswax in amount which is substantially in excess of its solubility in said furfural.

3. In the extractive distillation of unsaturated hydrocarbons with furfural as a solvent wherein the furfural becomes contaminated with foam-producing substances, the improvement which comprises suppressing foaming by admixing with the furfural used as the solvent beeswax in a concentration at least equal to 0.0635 weight per cent.

4. In the extractive distillation of unsaturated hydrocarbons with furfural as a solvent wherein the furfural becomes contaminated with foam-producing substances and wherein the temperature of the furfural is at least 145° F., the improvement which comprises suppressing foaming by admixing with the furfural used as the solvent beeswax in a concentration at least equal to 0.0635 weight per cent.



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