JOINT DISCUSSION*

MR. J. A. WOOD.[1]—Has anything been done on the thermal diffusion of wax?

MR. A. L. JONES (*author*).—We have thermally diffused waxes and know they are susceptible to fractionation, but we have done a poor job of analyzing the fractions we have obtained. There are components in waxes which can be fractionated but we do not know what they are.

MR. S. S. KURTZ.[2]—If you separate a saturated molecule averaging about 30 carbon atoms with 4 rings per molecule, would it fit in with your current thinking to believe that you have 3 of those rings in a condensed structure something like phenanthrene and one as an isolated cyclohexane ring? Does this fit your thinking, and can you prove it?

MR. F. W. MELPOLDER. (*author*)— We have made a limited number of experiments in which we believe molecules containing both condensed and noncondensed ring systems have been detected. Thermal diffusion apparently does not distinguish between cyclic compounds having different degrees of condensation. Mass spectrometer analyses of eicosane distillate fractions have indicated that tricyclic molecules existed having both completely condensed and partially condensed nuclei.

MR. B. A. ORKIN.[3]—Presently a lubricating oil is being marketed that has a viscosity index between 140 and 145 and a viscosity of 63 sec at 210F. I wonder if you have isolated from virgin petroleum any materials that would approach this marketed material in viscosity and viscosity index?

MR. MELPOLDER.—Our recent study of a medium-viscosity lubricating oil showed that one fraction had a viscosity index of 167 and a viscosity of 45 sec at 210 F. Another fraction had a viscosity index of 145 and a viscosity of 48 sec at 210 F. Since the viscosity of this lubricating oil charge stock was 62 sec at 210 F, it is expected that a heavier charge stock must be used to obtain fractions in the range of 140 to 145 viscosity index and viscosity of 63 sec at 210 F.

MR. JONES.—I am not sure I understand the question exactly, but you can make higher viscosity index fractions than those you mentioned, and isolate the fractions from petroleum in this viscosity range. But the thing responsible for viscosity index is entirely different. The molecular weight of the petroleum fraction of high viscosity index is about 400. In one case it is due to its isoparaffin structure. In the other case it is the influence of the long polymer on the ability of the

* This discussion is a joint discussion of A. L. Jones' paper, "New Thermal Diffusion Techniques Applicable to High-Boiling Petroleum Fractions," p. 83, and F. W. Melpolder, R. W. Sauer, and T. A. Washalls' paper, "The Separation of High-Boiling Petroleum Oils by Thermal Diffusion," p. 94.
[1] Cit-Con Oil Corp., Lake Charles, La.
[2] Sun Oil Co., Marcus Hook, Pa.

[3] Socony Mobil Oil Co., Inc., Paulsboro, N. J.

total mixture to flow at different temperatures.

MR. ORKIN.—Do I understand it is possible to isolate a fraction of viscosity up to 60 sec? In Table I of Mr. Jones' paper, the author has 46 sec, that is about 17 sec less than what I stipulated.

MR. JONES.—On the last chart one of the fractions I got had a viscosity index of 170 and a viscosity of 46 sec at 210 F.

MR. S. H. HASTINGS.[4]—In Table II of Mr. Melpolder's paper fluorenes are shown as one compound type. Were these identified as such or inferred from mass spectra? Also, dihydronaphthalenes.

MR. MELPOLDER.—In the calculation of mass spectra, a matrix was devised for the determination of 16 types of hydrocarbons in the high-molecular weight region. Basically, this was done by mass assignments according to the formula C_nH_{2n-z} by calibration with available pure compounds and other correlations. Since we do not have complete calibration information for the many types of compounds, it is not possible to differentiate between specific hydrocarbon structures having the same z value. Fluorenes, for example, having a z value of 16 cannot be positively identified as such if other structures also having a z value of 16 such as acenaphthalenes exist. Dihydronaphthalenes would be similarly grouped with other structures having a z value of 10. However, we have identified fluorenes in other stocks by ultraviolet analysis.

To what extent do gas bubbles in the column interfere with the efficiency of thermal diffusion separation? What is the best way to eliminate air from the sample and column during charging?

MR. JONES.—Gas bubbles do interfere with thermal diffusion operation. They can be eliminated when filling the columns by entering the material at the bottom rather than having the liquid dropping from the upper part to the bottom. This air will work itself out of the liquid. Usually it will take place in the first few hours of operation. In order to be sure that the column is free of bubbles, you simply release the uppermost port cap and allow the liquid in the reservoir to fill the column. If liquid comes out promptly you can be sure there is not much air in the system.

If you check it a day later and the liquid still comes out, you have no trouble with bubbles.

MR. MELPOLDER.—Initially, it was not too difficult to fill a column with sample such that the air was completely displaced. The trouble we have gotten into, especially with multi-column apparatus, was that gas seemed to be liberated not for hours but for days. Perhaps for six or seven days after starting a run a few cu cm of air would accumulate each day at the top of the column assembly. I suspect that this was due to dissolved air in the sample itself. So far, we have not been able to eliminate this.

MR. C. C. WARD.[5]—We had this problem of air in the sample and it has been our experience that it is not removed the first day of operation.

We have been operating two of our columns using a continuous takeoff rate of about 0.7 ml per day from the top and bottom of the column using motor-actuated hypodermic syringes. Under these conditions any gas at the top of the column is withdrawn and reduces the liquid withdrawal by the same amount.

The method that we are using at present to combat this difficulty is to charge the sample into a glass bulb attached to the charge line by a spherical joint in a horizontal position. The bulb is rotated on the joint to a vertical downward position and in this position it is chilled by surrounding it with a Dewar of liquid air. After the sample is chilled to prevent sample loss, a vacuum is applied to the column and to the sample container. The vacuum is then turned off and the sample allowed to warm somewhat. After this chilling, evacuation, and warmup are repeated three times, the sample and column are essentially air free. The sample bulb is then rotated around the joint to a vertical upward position and a slight positive pressure of helium is placed over the sample, after which the column is operated in the usual manner.

MR. MELPOLDER.—What types of thermal diffusion apparatus have been tested other than Clusius-Dickel column for laboratory separations?

MR. JONES.—There is such a variety of apparatus types a great deal of time could be spent discussing that alone. They have assumed almost every imaginable configuration.

MR. MELPOLDER.—What is the optimum annular space in a column of given length to give a sharp separation in a reasonable time?

MR. JONES.—There is an optimum for continuous operations and it depends on the length of the column. Fortunately, information on this whole subject has now been released and a presentation of it will be made at the Gordon Research Conference on Separation and Purification this summer (1957). I cannot give you any actual dimension, the mathematical treatment of the whole system will be given at this conference.

MR. C. B. WILLINGHAM.[6]—Would not this depend on the batch which is to be separated?

MR. JONES.—It would depend on what you are trying to do. If you have to do it within a given time, you cannot afford to have the spacing too narrow. The maximum separation is an inverse fourth power relationship between spacing and separation. The closer you get the walls together the greater the separation. Also, the longer you have to wait to get it. For continuous operation the optimum I was referring to is a wider space than in noncontinuous operations.

MR. WILLINGHAM.—I think some people are likely to be confused when we talk about batch separations in the Jones-Hughes column. This method can only demonstrate the separation you may expect on a continuous basis; that is, it will give you a top and bottom product in near maximum concentrations. Have you come up with any other name besides "batch" for this use of the Jones-Hughes column? If so, maybe it would straighten this out. (Mr. Melpolder published some time ago a batch separation procedure in which he fed to the top of the column and removed product only from the bottom. This gives a molecular type separation analogous to the molecular weight separation of analytical distillation.) (See authors' Ref. (7).)

MR. JONES.—I do not know who gave it the name of batch column; we call it static, because it is not continuous. I might mention we also have a design of apparatus in which we get twice the separation on a continuous basis that the same apparatus will give on a static basis.

MR. MELPOLDER.—I should like to ask Mr. Willingham what types of

barriers are suitable for packing in the thermal diffusion column? Have permeable membranes been used?

MR. WILLINGHAM.—In our packed concentric-tube columns we have used glass fiber packing. Actually, Mr. Jones should answer this question regarding membranes. However, we have both successfully used many types including wood, polyethylene, paper, and several others, and in a large range of pore diameters. So long as the liquid pressure on either side of the membrane is the same and you depend only on diffusion they are all right. However, for the case where there is a pressure difference across the membrane, we have found no satisfactory membrane that will allow thermal diffusion and yet stop pressure or mass flow.

MR. JONES.—Membrane stability is a problem. We have never found one to be entirely satisfactory from the standpoint of holding up for any length of time, nor well enough to be included in apparatus to be used over an extended period.

MR. MELPOLDER.—Are short microcolumns of practical value for additional separations of thermal diffusion fractions from larger columns?

MR. WARD.—We have been using a semi-micro thermal diffusion column of about 1 ml capacity to rerun fractions that we obtain from a standard Jones-Hughes column. This column has been used successfully to concentrate sulfur compounds from the bottom fraction from our larger columns. An indication of the efficiency of the column is in the separation of a 50-50 mixture of methylcyclohexane and n-heptane to better than 90 per cent of one of the components at each end of the column.

The column was made using a 2-ft length of 2-mm inside diameter glass tubing for the outside wall and a length of 0.058 in. stainless steel hypodermic tubing as the inside wall. This provides a 0.01 in. width annulus. A small voltage is applied across the stainless steel tubing so it is the hot wall, and the glass tubing, surrounded by a water jacket, is the cold wall. We do not know the differential across the column as we cannot measure the inside temperature. In operation the voltage is increased up to the incipient boiling point of the sample and then the voltage is reduced slightly.

A MEMBER.—In continuous operation of liquid thermal diffusion columns, is the feed always introduced at the vertical center of the column? If not, what factors influence or determine the location of feed?

MR. MELPOLDER.—We have done no work of that type. Mr. Jones may be better able to answer that question.

MR. JONES.—This information has not as yet been released.

MR. MELPOLDER.—To add a further comment to this question, we are concerned with the optimum point of feed to the multicolumn apparatus. We have made several tests by moving the connecting tubing to different ports along the column. The results so far are not sufficient to draw conclusions, but it does make a real difference as to where the feed line is placed. We expect to find out more about this shortly.

MR. H. C. RAMPTON.[7]—To what extent would the use of solvents facilitate or improve separation by thermal diffusion of the higher molecular weight components of petroleum?

MR. JONES.—The solid materials are difficult to process as they are. This type of apparatus requires that the material be liquid, and being

liquid for a lot of high-melting materials, you get the best thermal diffusion operation. Quite often, it is so high melting that it decomposes, may crystallize, and run into a lot of difficulty. Can you use solvents?

If the solid material consists of a few components, then the choice of solvent is extremely difficult. You must choose something which will diffuse in intermediate fashion between the components you wish to separate. It can be done, but it is difficult.

In many experiments our test mixture is a 50-50 volume mixture of alpha and beta methyl naphthalenes with cetane. In the presence of cetane, the alpha and beta methylnaphthalene isomers go to the bottom of the column. In the presence of cetane, both isomers behave alike. If you remove the cetane and charge the apparatus with the two isomers of methylnaphthalene, they separate from each other. In this case the solvent retards the separation of the individual isomers.

You can separate petroleum residual fractions by diluting them with naphtha fractions from the same crude oil. The naphtha has the same hydrocarbon types as does the residual. Since the process separates on the basis of the types of configurations and not in terms of molecular weight, you will find that the high molecular weight and long chain compounds will go along with low molecular weight chain compounds. You will get fractionation according to molecular type. You will find some high molecular weight components at both the top and bottom. When using a solvent that has the same molecular type, regardless of size, we do not separate solvents from solute.

MR. MELPOLDER.—We have only a little experience in combining thermal diffusion with mixtures of oil and

selective solvents. We had hoped that the movement of different hydrocarbons in the column could be influenced by the presence of a highly selective solvent. It was found, however, that although the solvent quickly moved to the bottom of the column, no unusual separation of the hydrocarbon mixture occurred.

MR. WARD.—Does anyone have experience with the operation of thermal diffusion columns under pressure, thereby permitting higher operating temperatures?

MR. JONES.—Drickamer, at the University of Illinois, has operated at 10,000 atmos. We have not gone to pressures that high, but we have pressurized columns to 200 lb. That is a good way to go above the normal boiling point—just pressurize.

MR. CALVIN F. RUEPING.[8]—Is thermal diffusion an instantaneous migration to hot and cold surfaces? In other words, is the separation instantaneous while the gravitational migration is the time-consuming portion to steady state in a Clusius and Dickel column?

MR. JONES.—It is not instantaneous; but it is fast. You get a good concentration gradient between walls in a matter of minutes, but it may be a matter of hours before that concentration difference can migrate to the ends of the apparatus of the type we are discussing.

MR. B. J. MAIR.[9]—For the branched paraffin-cycloparaffin portion, thermal diffusion tends to concentrate the branched paraffins in the first fractions, the material becoming richer in multiring cycloparaffins as successive fractions are withdrawn. However, branched paraffins seem to be present, though in decreasing amounts, from

the first fraction throughout most of the range of fractions. Since the separations obtained with thermal diffusion depend largely on the shape of the molecules, it is reasonable to suppose that the nature of the branched paraffins will change throughout a thermal diffusion separation, with the more highly branched material concentrating with the multiring cycloparaffins. Is there any evidence from spectroscopic measurements to indicate that this is actually taking place?

MR. MELPOLDER.—The nature of the branched paraffins of the type discussed at this symposium certainly has much to do with the separation process in the thermal diffusion column. I have already mentioned the fact that isoparaffins and monocycloparaffins did not separate from each other to any great extent in thermal diffusion. This may be due to the similarity in structure between the isoparaffins and the long paraffin chain on the cycloparaffin ring. Unfortunately, we have not been able to make the necessary mass spectrometer study to shed light on this question. Some day, perhaps, when more background is accumulated, such that fragmentation spectra can be better correlated with structure, we might be able to determine the degree of branchiness of the isoparaffins.

MR. JONES.—Is thermal diffusion effective in separating the components of vegetable oils and other biological substances?

MR. MELPOLDER.—If I knew more about the nature of these materials, I might hazard a guess. Actually, I do not know enough about this.

MR. JONES.—Can thermal diffusion be used for the concentration of isotopes and how does it compare with other ways of concentrating them?

MR. J. K. FOGO.[10]—Thermal diffusion is one of the ways of concentrating

isotopes. It was originally used for this purpose by Clusius and Dickel to separate the isotopes of chlorine (gas). It has also been used quite successfully to separate carbon-13 from ordinary carbon in the form of gaseous thermal diffusion of methane. Since liquid thermal diffusion appears to separate mixtures according to molecular shape rather than by molecular weight, any isotope separation in liquids of even low molecular weight would be unexpected, and certainly would not occur in anything like the petroleum oils we have been discussing. So far as I know, thermal diffusion is not competitive with other methods for commercial isotope concentration.

MR. KURTZ.—When isotope work was just getting under way Houdry and Sun Oil did a little work on oxygen-18. It looked as though thermal diffusion would be a good way to separate oxygen-18. Sun Oil did get as far as the pilot plant stage on oxygen-18. When other isotopes became relatively plentiful, it became clear that it was not such a good idea. The work stopped right there.

A MEMBER.—Is it possible to predict from the properties of a mixture whether or not thermal diffusion will be effective in producing separations?

MR. JONES.—There is no nonempirical method of predicting thermal diffusion separations of simple mixtures. Drickamer and co-workers at the University of Illinois have related separation tendencies to the activation energies required for a given species of molecule to move from one position to another within a liquid medium. The activation energies may be computed from measurable properties such as the viscosities of pure components at two different temperatures and their molar volumes. The energy data are applied to thermodynamic relationship developed by Denbigh in England.