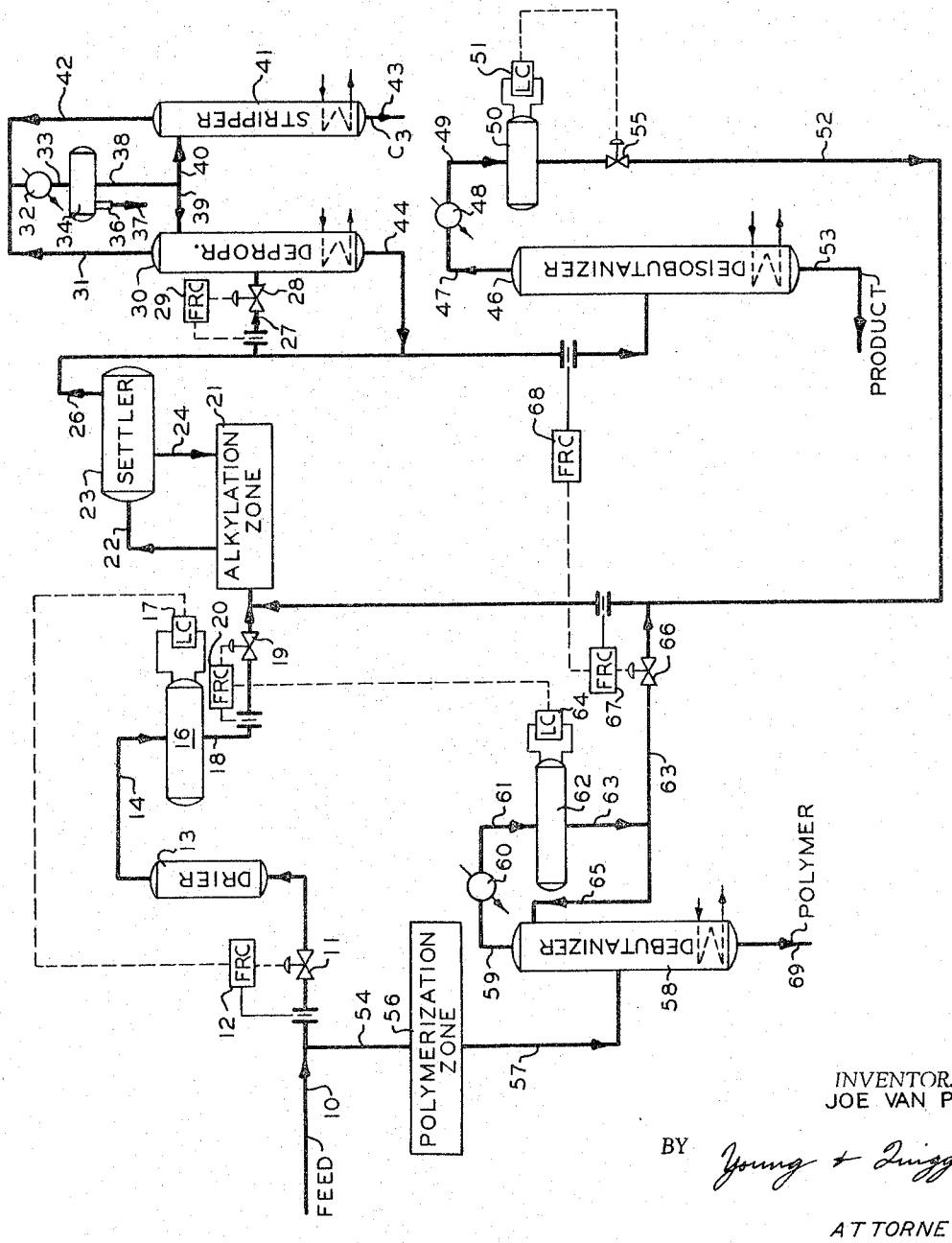
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CONTROLLING A COMBINED ALKYLATION POLYMERIZATION PROCESS TO INCREASE THE ALKYLATE

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CONTROLLING A COMBINED ALKYLATION POLYMERIZATION PROCESS TO INCREASE THE ALKYLATE

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This invention relates to an improved process and apparatus therefor wherein the conversion of olefin hydrocarbons into valuable gasoline boiling-range hydrocarbons is increased. In a specific aspect, this invention relates to an improved method of and apparatus for controlling a combined alkylation and polymerization process.

Alkylation and polymerization processes are conventionally employed to produce valuable gasoline boiling-range hydrocarbons from olefins. The production of alkylate is generally preferred as the spread (representative of value) between the octane of alkylate measured by the motor method and the octane of alkylate measured by the research method is less than that for the polymer prepared from the same olefin feed.

In the petroleum industry olefin feed to polymerization and alkylation processes conventionally is obtained from catalytic hydrocarbon cracking processes. Generally, the relative concentration of butylenes, isobutane and propylene in the olefin feed are constantly changing. Fluctuations in the feed composition are undesirable in that the alkylating agent (isobutane) to olefin feed ratio to an alkylation process should be maintained substantially constant. A low isobutane to olefin feed ratio will result in a low alkylate product yield and low quality, while a high isobutane to olefin feed ratio will result in the loss of isobutane, the isobutane being withdrawn from the process with the alkylate product. The latter is undesirable as conventionally the quantity of isobutane available is a limiting factor in the production of alkylate.

Accordingly, an object of my invention is to provide an improved method of and apparatus for controlling an olefin hydrocarbon conversion process.

Another object of my invention is to provide an improved method of and apparatus for controlling a combined alkylation-polymerization process to increase the production of alkylate.

Another object of my invention is to provide an improved method of and apparatus for controlling a combined alkylation-polymerization process so as to produce a higher yield of alkylate of high octane.

Other objects, advantages and features of my invention will be readily apparent to those skilled in the art from the following description and the appended claims.

I have by my invention provided a method of and apparatus for controlling a combined alkylation-polymerization process wherein the feed to the alkylation step is controlled to increase the production of alkylate and the isobutane to olefin feed ratio to the alkylation step is maintained more nearly constant, said olefin feed comprising butylenes and propylene.

The drawing is a schematic representation of the invention alkylation-polymerization process control system.

Referring to the drawing, a substantially sulfur-free feed stream comprising isobutane, butylenes, propylene and minor concentrations of propane is passed through conduit means **10**, divided, and a portion passed to a polymerization zone **56** via conduit means **54**. The remainder of the feed stream is passed to a conventional drier **13** and from drier **13** to an accumulator **16** via conduit means **14**. The dried feed is withdrawn from accumulator **16** via conduit means **18** and passed to a conventional alkylation zone **21** in combination with a recycle stream, hereinafter described, and passed to conduit means **18** via conduit means **52**.

Within alkylation zone **21**, the hydrocarbon feed is contacted with a conventional alkylation catalyst such as hydrofluoric acid, phosphoric acid or sulfuric acid. The acid to hydrocarbon feed volume ratio is conventionally maintained in the range of about 10:1 to 1:4. The temperature of alkylation zone **21** is maintained in the range of between about 60–120° F. and the pressure within alkylation zone **21** is sufficient to maintain a liquid phase reaction. An effluent stream is withdrawn from alkylation zone **21** via conduit means **22** and passed to a phase settler **23**.

Within settler **23**, the effluent is permitted to settle into a hydrocarbon phase and an acid phase. The acid phase is withdrawn from settler **23** via conduit means **24** and recycled to the alkylation zone. The hydrocarbon phase is withdrawn from settler **23** via conduit means **26**.

A portion of the hydrocarbon phase withdrawn from settler **23** is passed via conduit means **27** to a depropanizer column **30**. Within depropanizer **30**, propane is separated from the feed stream and withdrawn from depropanizer **30** via conduit means **31**. The remainder of the feed stream is withdrawn as a liquid from depropanizer **30** via conduit means **44** and combined with the remainder of the hydrocarbon phase withdrawn from settler **23**, the combined hydrocarbon stream passed to deisobutanizer column **46**. The top temperature and pressure of depropanizer **30** is conventionally in the range of 110–130° F. and in the range of 250–300 p.s.i.g., respectively. The vaporous stream withdrawn from depropanizer **30** via conduit means **31** is condensed via heat exchange means **32** and passsed to an accumulator **34**. Acid catalyst and water withdrawn from settler **23** with the hydrocarbon phase settles in acid leg **35** and is withdrawn from accumulator **34** via conduit means **37**. The condensed propane is withdrawn from accumulator **34** via conduit means **38** and a portion of the withdrawn propane passed as reflux to depropanizer **30** via conduit means **39**. The remainder of the propane stream is passed via conduit means **40** to a stripper column **41**.

Within stripper column **41**, the remaining acid is stripped from the propane and withdrawn as a vaporous phase via conduit means **42**. The vaporous acid phase is condensed by heat exchange means **32** and passed via conduit means **33** to accumulator **34**. An acid-free propane product stream is withdrawn from stripper **41** via conduit means **43**. The bottom temperature and pressure of stripper **41** is conventionally in the range from about 105–125° F. and from about 255–305 p.s.i.g., respectively.

Deisobutanizer column **46** is conventionally operated at a top temperature and pressure in the range of 130–160° F. and in the range of 100–130 p.s.i.g., respectively. A vaporous stream comprising isobutane and propane is withdrawn from deisobutanizer **46** via conduit means **47**, condensed via heat exchange means **48** and passed via conduit means **49** to an accumulator **50**. A liquid product stream comprising n-butane and alkylate is withdrawn from deisobutanizer **46** via conduit means **53** and passed to a conventional means of separating the n-butane from the alkylate such as a fractionation zone. A liquid isobutane stream is withdrawn from accumulator **50** via conduit means **52** and recycled to alkylation zone **21** via conduit means **18**.

Within polymerization zone **56**, the feed material is contacted with a conventional polymerization catalyst such as a catalyst selected from the group comprising phosphoric acid and copper pyrophosphate. The temperature and pressure of polymerization zone **56** is conventionally maintained in the range of 300–450° F. and in the range of 500–800 p.s.i.g., respectively. An effluent

stream comprising isobutane, n-butane, propane and polymer is withdrawn from polymerization zone 56 via conduit means 57 and passed to a debutanizer column 58.

Debutanizer column 58 is operated at a top temperature and pressure in the range of 110–150° F. and in the range of 50–100 p.s.i.g., respectively. A vapor stream comprising isobutane, n-butane and propane is withdrawn from debutanizer 58 via conduit means 59, condensed via heat exchange means 60 and passed via conduit means 61 to an accumulator 62. A polymer product stream is withdrawn from debutanizer 58 via conduit means 69. Condensed liquid is withdrawn from accumulator 62 via conduit means 63 and a portion of the condensed liquid recycled via conduit means 65 as reflux to debutanizer 58. The remainder of the condensed liquid withdrawn from accumulator 62 is passed via conduit means 63 to conduit means 52 wherein said condensed liquid is combined with the recycle isobutane stream recycled to alkylation zone 21 via conduit means 18.

Having described the process flow, the inventive control system will now be described. The rate of flow of feed to drier 13 is controlled by a conventional flow-recorder-controller 12 opening or closing valve 11 responsive to a flow measurement within conduit 10 and a reset signal transmitted from a conventional liquid level controller 17. Liquid level controller 17 senses the liquid level within accumulator 16, compares this with a set point, and transmits a reset signal to flow-recorder-controller 12 responsive thereto. The rate of flow of feed to drier 13 is thus controlled responsive to the liquid level within accumulator 16. For example, a liquid level in accumulator 16 above the set point level will result in the rate of flow through valve 11 being reduced.

The rate of flow of liquid from accumulator 16 to alkylation zone 21 via conduit means 18 is controlled by a conventional flow-recorder-controller 20. Flow-recorder-controller 20 opens or closes valve 19 responsive to a rate of flow sensing means in conduit 18 and to a reset signal transmitted by a conventional liquid level controller 64. Liquid level controller 64 senses the liquid level within accumulator 62, compares this measurement with a set point, and transmits a reset signal to flow-recorder-controller 20 responsive thereto. Thus, the rate of flow of liquid from accumulator 16 to alkylation zone 21 is controlled responsive to the liquid level within accumulator 62. For example, a liquid level in accumulator 62 above the set point level will result in the rate of flow through valve 19 being increased.

The rate of flow of the hydrocarbon phase withdrawn from settler 23 to depropanizer 30 is controlled by a conventional flow-recorder-controller 29. Flow-recorder-controller 29 opens or closes valve 28 responsive to a rate of flow sensing means within conduit 27 and responsive to a set point signal representative of the rate of flow to depropanizer 30 required to prevent propane build-up within alkylation zone 21.

The rate of flow of feed to deisobutanizer 46 is sensed by a conventional flow-recorder-controller 68, compared with a set point representative of a desired rate of flow, and a reset signal responsive thereto transmitted to a conventional flow-recorder-controller 67. The rate of flow of liquid through conduit 63 to conduit 52 is controlled by flow-recorder-controller 67. Flow-recorder-controller 67 opens and closes valve 66 responsive to a rate of flow sensing means in conduit 52 and responsive to a reset signal received from flow-recorder-controller 68. For example, a rate of flow measurement by flow-recorder-controller 68 less than the set point rate of flow will result in the rate of flow through valve 66 being increased. The rate of withdrawing isobutane from accumulator 50 is controlled by a conventional liquid level controller 51. Liquid level controller 51 senses the liquid level within accumulator 50, compares this with a set point, and opens or closes valve 55 responsive thereto. Thus, the inventive control system operates to maintain the rate of flow to deisobutanizer 46 at a desired or maximum level.

The inventive control system can better be understood by referring to a specific example. Assume that the feed to the combined alkylation-polymerization process decreases. For a period of time the same quantity of feed will pass to alkylation zone 21 with less feed passing to polymerization zone 56. As the feed to polymerization zone 56 has been decreased, the liquid level within accumulator 62 will begin to fall. This decrease in liquid level within accumulator 62 results in liquid level controller 64 transmitting a reset signal to flow-recorder-controller 20, thereby reducing the rate of liquid flow from accumulator 16 to alkylation zone 21.

The decrease in flow of liquid from accumulator 16 causes the liquid level in accumulator 16 to rise, and this raise in the liquid level within accumulator 16 results in liquid level controller 17 transmitting a reset signal to flow-recorder-controller 12, thereby decreasing the flow of feed through conduit 10 to drier 13. The decrease in the rate of feed flow to drier 13 will result in the rate of flow of feed to polymerization zone 56 being increased and this in turn will increase the liquid level within accumulator 62.

While the decreased feed is being charged to alkylation zone 21, the charge to deisobutanizer 46 begins to fall off, or is reduced (the charge to depropanizer 30 being a preset constant). The decrease in the rate of flow to deisobutanizer 46 is sensed by flow-recorder-controller 68 which in response thereto transmits a reset signal to flow-recorder-controller 67, thereby increasing the rate of liquid flow from accumulator 62 to conduit means 52. This last control action brings the charge to deisobutanizer 46 back to its preset or desired level. With the increased rate of flow of liquid from accumulator 62, the level within accumulator 62 again starts to fall which again controls the rate of flow of liquid from accumulator 16 to alkylation zone 21. This ultimately results in a balance between the alkylation and polymerization process steps so that increased alkylate is produced for the available isobutane.

A novel feature of the inventive control system is readily apparent when it is noted, for example, that if the liquid level within accumulator 62 is reduced, the first change in the control system, after the feed to alkylation zone 21 is reduced, tends to reduce the liquid level within accumulator 62 even more. The decrease in feed to alkylation zone 21 is noted as also a decrease in the feed to deisobutanizer 46 almost immediately. The time lag through the polymerization zone 56 does not permit an increase in the liquid level within accumulator 62 immediately as the feed to alkylation zone 21 is decreased. The change in feed rate of flow to deisobutanizer 46 is sensed immediately and results in a further lowering of the level in accumulator 62. This is reversed to conventional methods of control.

After a time lag, the increase in feed to polymerization zone 56 results in an increase in liquid level in accumulator 62. This increase in liquid level effects an increase in the charge to alkylation zone 21 which in turn decreases the charge to polymerization zone 56, and the control system readjusts itself, ultimately balancing the alkylation and polymerization processes so that increased alkylate is produced. The increased feed to the liquid full alkylation system now containing the additional olefin will employ more isobutane in the alkylation reaction and shrinkage due to alkylate production is noted in the feed to deisobutanizer 46. This lower deisobutanizer feed rate again increases the liquid flow from accumulator 62 to the isobutane recycle stream flowing through conduit 52. The increased isobutane recycle ultimately increases the liquid level in accumulator 50 and the level control thereon increases the flow of isobutane recycle therefrom. This in turn reduces the flow of liquid from accumulator 62 to the recycle stream, allowing the liquid level in accumu-

lator 62 to again start to rise which will increase the alkylation zone feed rate.

The inventive control system balances the shrinkage due to production of alkylate (proportional to olefin present and proportional to the isobutane to olefin ratio) against feed to alkylation zone 21 plus recycle isobutane so that increased alkylation is effected for the available isobutane.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure and discussion without departing from the spirit or scope thereof.

I claim:

1. A process which comprises passing at least a portion of a hydrocarbon feed to an alkylation zone, said hydrocarbon feed comprising isobutane and an olefin selected from the group consisting of butylenes and propylene, passing the remainder of said hydrocarbon feed to a polymerization zone, passing a hydrocarbon effluent from said alkylation zone to a first fractionation zone, recycling an isobutane stream from said first fractionation zone to said alkylation zone, withdrawing an alkylate product stream from said first fractionation zone, passing a hydrocarbon effluent from said polymerization zone to a second fractionation zone, withdrawing a polymer product stream from said second fractionation zone, passing an isobutane stream from said second fractionation zone to a storage zone, passing an isobutane stream from said storage zone to said alkylation zone, measuring the rate of flow of hydrocarbon effluent to said first fractionation zone, comparing the thus measured rate of flow with a signal representative of the desired rate of flow of said hydrocarbon effluent to said first fraction zone, manipulating the rate of flow of isobutane from said storage zone to said alkylation zone responsive to said comparison to maintain the actual rate of flow of said hydrocarbon effluent to said first fractionation zone substantially equal to said desired rate of flow, and varying the quantity of said portion of said hydrocarbon feed passed to said alkylation zone responsive to the liquid level in said storage zone.

2. A process which comprises passing at least a portion of a hydrocarbon feed to an alkylation zone, said hydrocarbon feed comprising isobutane and an olefin selected from the group consisting of butylenes and propylene, passing the remainder of said hydrocarbon feed to a polymerization zone, passing a hydrocarbon effluent from said alkylation zone to a first fractionation zone, recycling an isobutane stream from said first fractionation zone to said alkylation zone, withdrawing an alkylate product stream from said first fractionation zone, passing a hydrocarbon effluent from said polymerization zone to a second fractionation zone, withdrawing a polymer product stream from said second fractionation zone, passing an isobutane stream from said second fractionation zone to a storage zone, passing an isobutane stream from said storage zone to said alkylation zone, measuring the rate of flow of hydrocarbon effluent to said first fractionation zone, comparing the thus measured rate of flow with a first signal representative of the desired rate of flow of said hydrocarbon effluent to said first fractionation zone and establishing a second signal representative of said comparison, measuring the combined rate of flow of said isobutane streams from said first fractionation zone and said storage zone to said alkylation zone and establishing a third signal representative of the thus measured combined rate of flow, manipulating the rate of flow of said isobutane stream from said storage zone responsive to said second and third signals, and varying the quantity of said portion of said hydrocarbon feed passed to said alkylation zone responsive to the liquid level in said storage zone.

3. The process of claim 2 to include passing at least a portion of the hydrocarbon effluent withdrawn from said alkylation zone to a third fractionation zone, withdrawing propane from said third fractionation zone, passing a liquid stream from said third fractionation zone to said first fractionation zone, and manipulating the rate of flow of said hydrocarbon effluent to said third fraction zone so as to prevent the build-up of propane in said alkylation zone.

References Cited by the Examiner

UNITED STATES PATENTS

2,211,747	8/1940	Goldsby et al.	260—683.15
2,881,235	4/1959	Van Pool	260—683.48
3,002,818	10/1961	Berger	260—683.48 X

OTHER REFERENCES

"Hydrofluoric Acid Alkylation" published by the Phillips Petroleum Co., Bartlesville, Okla., 1946, pages 22-24 and Figure 15 relied on.

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