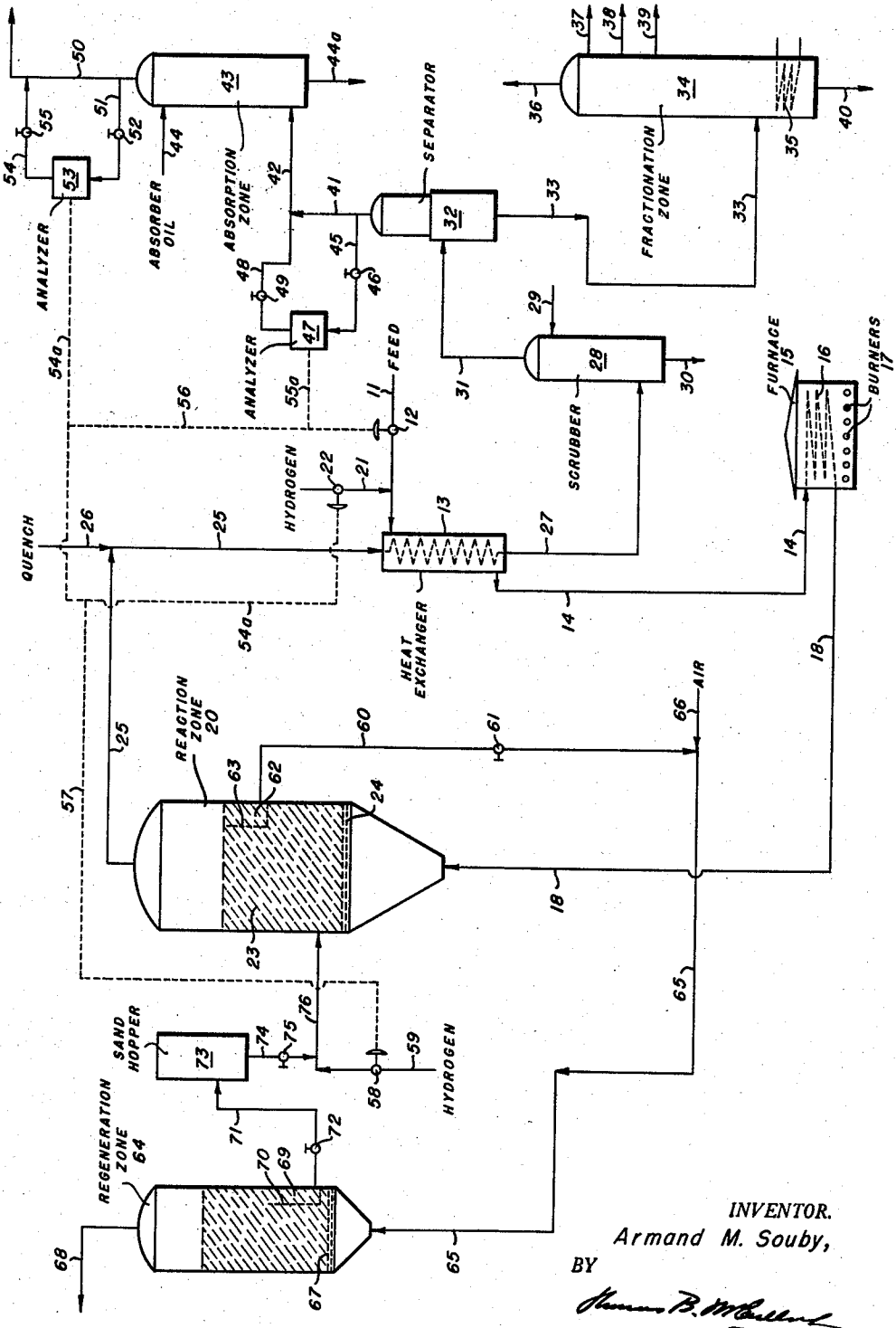
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HYDRODEALKYLATION OF HYDROCARBONS

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The present invention is directed to a method for dealkylating alkylated aromatic hydrocarbons. More particularly, the invention is directed to the thermal dealkylation of alkylated aromatic hydrocarbons. In its more specific aspects, the invention is directed to the thermal dealkylation of alkylated aromatic hydrocarbons at an elevated temperature in the presence of hydrogen.

The present invention may be briefly described as a method for thermally dealkylating an alkylated aromatic hydrocarbon in which the formation of coke is controlled and suppressed.

The alkylated aromatic hydrocarbon feed is heated in a thermal dealkylation zone in the presence of hydrogen to a temperature within the range between about 1100° and about 1600° F. and at a pressure within the range between about 400 and about 1000 pounds per square inch gauge for a time within the range of about 2 and about 120 seconds in the presence of a fluidized bed of catalytically inert finely divided solids in which a liquid product and a residue gas are produced. In the present invention the residue gas is flowed through a sensing zone to obtain a signal which is a function of the methane to hydrogen ratio in the residue gas. This signal is then employed to vary the ratio of hydrogen and alkylated aromatic hydrocarbon feed in the thermal reaction zone to provide a methane to hydrogen ratio in the residue gas such that the ratio of the equilibrium methane concentration to the actual methane concentration is above about 1.7 times the thermodynamic equilibrium ratio.

The finely divided solid employed in the bed may have a particle size in the range from about 100 to about 400 mesh and suitably may be alpha alumina, quartz, Carborundum, mullite, which is a silica-alumina, and the like.

The amount of hydrogen employed may be within the range of 6000 to 12,000 standard cubic feet per barrel of alkylated aromatic hydrocarbon feed, depending upon the hydrogen purity and operating severity. While pure hydrogen may be employed, a hydrogen-containing gas such as a catalytic reformer tail gas may also be used in suitable amount. Preferred ranges may be from 7000 to 8000 standard cubic feet of pure hydrogen per barrel of alkylated aromatic feed, or from 11,000 to 13,000 standard cubic feed of reformer tail gas containing 75 percent hydrogen per barrel of alkylated aromatic feed.

The present invention, as stated, is suitably conducted at a temperature within the range from about 1100° to about 1600° F. with a preferred temperature within the range of about 1250° to about 1350° F. Desirable results are obtained at about 1320° F. Pressures may range from about 400 to about 1000 pounds per square inch gauge with a preferred range from about 400 to about 700 pounds per square inch gauge. Satisfactory and desirable results are obtained at about 600 pounds per square inch gauge. Contact times may range from about 2 to about 120 seconds with good results being obtained at contact times of 2 to about 60 seconds.

The feed stocks employed in the practice of the present invention may be any alkylated aromatic hydrocarbon boiling within the range from about 200° to about 750° F., alkylated hydrocarbons such as alkyl benzenes such as illustrated by toluene, xylenes, ethyl benzene, mesitylene, and the like, and alkyl naphthalenes are illustrative desirable feed stocks. The alkyl naphthalenes may be illustrated by methyl naphthalenes, dimethylnaphthalenes, ethylnaphthalenes, trimethylnaphthalenes, methyl-ethylnaphthalenes and higher molecular weight homologues but other alkylated aromatic hydrocarbons may be used. For example, the present invention may suitably be practiced with alkylated aromatic hydrocarbons in the gasoline and kerosene boiling ranges.

The sensing zone employed in the present invention to obtain a signal which is a function of methane to hydrogen ratio may be any sensing zone which will indicate the relative amounts of hydrogen and methane. For example, the sensing zone may suitably be a mass spectrometer or may be an indicating or recording gas gravitometer. Other sensing zones such as a gas adsorption chromatographic apparatus, a thermal conductivity cell, or an effusiometer may be employed. A signal is obtained from the sensing zone which is a function of the methane to hydrogen ratio.

The present invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode.

Referring now to the drawing, a feed aromatic hydrocarbon of the nature illustrated is introduced into the system by line **11** controlled by valve **12** and a hydrogen-rich gas is introduced into line **11** by line **21** controlled by valve **22**. The aromatic hydrocarbon and the hydrogen-rich gas are mixed in line **11** and introduced into a heat exchanger **13** wherein the temperature of the total feed is raised to a temperature within the range between about 400° F. and 800° F. The total feed at this temperature is withdrawn from the heat exchanger **13** by line **14** and may be introduced thereby into a heater or furnace **15** and flows through coil **16** wherein it is heated to a temperature within the range between about 700° F. and 900° F. by means of heat provided by burners **17**. The heated feed in a vaporized condition is withdrawn by way of line **18** from furnace **15** and introduced into a reaction zone **20**. In the reaction zone **20**, the preferred reaction temperature of 1250° F. to 1350° F. is maintained by the highly exothermic reactions of hydrodealkylation and hydrocracking. Alternatively, the feed aromatic hydrocarbon and the hydrogen-rich gas may be preheated separately and combined before being introduced at the proper temperature into the reaction zone.

A fluidized bed **23** is maintained in reaction zone **20** of finely divided catalytically inert solids of the type mentioned before. The bed **23** is maintained above a reactor grid **24**. In reaction zone **20** the reaction takes place wherein in accordance with the present invention the alkylated aromatic hydrocarbons are dealkylated to form substantially only the desired aromatic hydrocarbons and hydrogen and methane. The products of the dealkylation reaction are withdrawn from reaction zone **20** by way of line **25** and are quenched in line **25** by means of a quench oil introduced by line **26**. This quench oil may suitably be an oil such as the bottoms stream leaving fractionator **34** through line **40**. The quenched product in line **25** at a temperature within the range of about 700° F. to 1000° F. is then passed through heat exchanger **13** in heat exchange with the feed which further reduces the temperature to approximately 300° F. The cooled product is then introduced by way of line **27** into a scrubbing zone **28** wherein the quenched and cooled product is scrubbed with a heavy oil, such as recycled slurry oil from line **30** leaving scrubber **28**, introduced by line **29**. This scrubbing operation in zone **28** serves

to remove any finely divided catalytically inert solids carried over with the reaction product. The oil and the solids are discharged by way of line **30** from scrubber **28**. The excess slurry oil from line **30** may be filtered in a filter zone not shown and introduced into line **31** ahead of separator **32** in order to recover all of the desired product, while the catalytically inert solids recovered by filtration may be discarded. The reaction products are withdrawn from scrubber **28** by way of line **31** into a separation zone **32** in which a separation is made between the gaseous products and the liquid products. The liquid products are withdrawn from separator **32** by way of line **33** and introduced thereby into a fractional distillation zone **34**. Fractional distillation tower **34** is shown as a single fractional distillation tower which suitably may include a plurality of fractional distillation towers, each equipped with internal vapor-liquid contacting means, such as bell cap trays and the like, means for inducing reflux and means for condensing and cooling the fractionated products. In short, zone **34** will include all auxiliary equipment necessarily found in the modern distillation tower.

In zone **34**, temperature and pressure conditions are adjusted by heating means illustrated by steam coil **35** such that light hydrocarbons are removed from zone **34** by line **36** and the dealkylated hydrocarbons are withdrawn by lines **37**, **38**, and **39**. Heavier products are discharged by line **40**.

The gaseous products from separator **32** are withdrawn therefrom by line **41** and introduced by line **42** into an absorption zone **43** into which absorber oil is introduced by line **44** to contact countercurrently the residue gas introduced by line **42**. The absorber oil may suitably be a stream from fractionator **34** such as one of the product streams from lines **37**, **38**, **39**, or **40**.

The absorption zone **43** is operated under suitable conditions of temperature and pressure to absorb hydrocarbons, such as propane, propylene, butanes, butylenes and heavier hydrocarbons while ethane and lighter hydrocarbons including hydrogen are not absorbed. The enriched absorption oil is discharged from zone **43** by line **44***a* for recovery of the absorbed hydrocarbons and for stripping of the absorber oil for re-use in the process. The enriched absorption oil from line **44***a* may conveniently be introduced into line **33** ahead of fractionator **34** wherein it will be stripped for re-use and the absorbed hydrocarbons recovered.

Line **45** controlled by valve **46** connects to line **41** and to a sensing means or an analyzer **47** to allow the residue gas in line **41** to pass therethrough and be discharged by way of line **48** controlled by valve **49** back into line **42**.

Provision of analyzer or sensing means **47** allows a portion of the residue gas in line **41** to be routed through the analyzer **47** and back into line **42**.

The unabsorbed residue gas from absorption zone **43** is discharged therefrom by way of line **50** and may be discarded or recycled to the process as a hydrogen-containing gas.

Connected to line **50** is line **51** controlled by valve **52** which leads to an analyzer or sensing means **53** of the type described. Line **54** controlled by valve **55** connects the analyzer **53** back into line **50** such that the residue gas may be circulated through the analyzer **53**.

The analyzers **47** and **53** suitably connect by electrical leads **54***a*, **55***a*, **56**, and **57** to valve **22** in line **21**, valve **12** in line **11** and to valve **58** in line **59**.

The operation of the reaction zone **20** is such that the heated feed is introduced by means of line **18** in admixture with hydrogen from line **21** into the bed **23** of finely divided catalytically inert solids in reaction zone **20**. From time to time the catalytically inert solids may become fouled with carbonaceous deposits and it is desirable to replace a portion of the catalytically inert solids. To this end, a portion of the inert solids is withdrawn from zone **20** by line **60** controlled by valve **61**. Line **60** leads into the zone **20** and connects into an annular section **62** defined by the walls **63**.

The inert solids in line **60** are carried to a regeneration zone **64** by way of line **65** connected thereto into which air is introduced by way of line **66** to support a combustion operation in zone **64** above the grid plate **67**.

The combustion operation burns off the carbonaceous matter from the catalytically inert solids at a temperature in the range from 900° to 1500° F. and a combustion product flue gas is withdrawn from zone **64** by line **68**.

The burned off catalytically inert solids are withdrawn from zone **64** through a zone **69** of zone **64** defined by an annular wall **70**. Line **71** controlled by valve **72** connects into zone **69**. Line **71** also connects into a hopper for catalytically inert solids **73** which is connected to line **76** by way of line **74** controlled by valve **75**.

In operating the present invention, any withdrawn catalytically inert solids containing carbonaceous material may be replaced by fresh or regenerated catalytically inert solids from hopper **73** by way of line **74** controlled by value **75**. When catalytically inert solids are added, hydrogen is introduced by line **59** controlled by valve **58** to carry the catalytically inert solids through line **76** to the bed **23**. Hopper **73** is capable of being operated at the pressure of the reaction zone **20** while catalytically inert solids are being added.

Hydrogen is admixed with the feed stock as has been described during the operation but hydrogen is added to line **76** only when it is desired to add catalytically inert solids from hopper **73**.

It is to be emphasized that catalytically inert solids may be withdrawn from zone **20** and added to zone **20** only at relatively long intervals as carbonaceous deposits accumulate on the catalytically inert solids. The amount withdrawn and the amount added may comprise only about 5% by weight of the amount of catalytically inert solids in the bed **23**. The interval of time at which catalytically inert solids are withdrawn and added may range from about 1 to 20 days. In short, the withdrawal and addition of catalytically inert solids is only at infrequent intervals. The withdrawn catalytically inert solids containing carbonaceous material may be cooled and discarded rather than regenerated if desired.

In accordance with the present invention formation of carbon and coke in the reaction zone **20** and in the transfer line **25** is controlled and suppressed by maintaining a ratio of the thermodynamic equilibrium concentration of methane (calculated on the basis of the concentration of hydrogen present) to the actual concentration of methane in the residue gas above a value of about 1.7, under the conditions of reaction zone **20**.

In order to illustrate the invention further, hydrodealkylation operations were conducted on a fraction boiling above 400° F. of kerosene sulfur dioxide extract which contained about 86% of alkylated aromatics. This kerosene extract was heated to about 800° F. and introduced into a reaction zone containing a fluidized bed of silica sand. The exothermic heat of reaction in the reaction zone maintained the temperature of reaction at about 1300° F. Hydrogen-rich gas was introduced with hydrocarbon feed to provide the required amount of hydrogen. Runs were conducted at 1270° to 1345° F., 600 pounds per square inch gauge and at 50 to 60 seconds residence time with from 6600 to 9800 standard cubic feet of hydrogen per barrel of feed being employed. The hydrogen employed contained between about 70 and about 79% H_2, the other components being methane and heavier hydrocarbons.

In these operations, coking was experienced in the reaction zone. In one of the runs at 1320° F. and 600 pounds per square inch gauge, it was found that the concentration of hydrogen in the residue gas was 32.3 mole percent and the concentration of methane was 47.7 mole

percent. The thermodynamic equilibrium concentration corresponding to the actual hydrogen concentration was 45.1 mole percent. The ratio of the equilibrium methane concentration to the actual methane concentration was 0.95. In this run the operation had to be terminated after 10 hours due to coking.

In another run with the same feed stock and 600 pounds per square inch gauge, the residue gas contained 35.6 mole percent hydrogen and 44.7 mole percent of methane. The thermodynamic equilibrium concentration of the methane corresponding to the hydrogen was 56.5 mole percent. The ratio of equilibrium methane concentration to the actual methane concentration was 1.26. This run had to be terminated after 12 hours due to coking.

It has been observed that the only hydrocarbon in the product under conditions existing at the reaction zone outlet which may be thermodynamically stable is methane. In the presence of sufficient hydrogen to make methane thermodynamically stable, the heavier hydrocarbons decompose and result in the formation of methane. In the presence of smaller quantities of hydrogen than are necessary to make methane thermodynamically stable, the decomposition reaction results in the formation of carbon and hydrogen. This carbon deposits on the walls, lines and in the reaction zone and makes the operation inoperable if allowed to continue. A measure of the ability of hydrogen to prevent coking is the degree of approach of the partial pressure of methane actually present to the partial pressure of methane that exists in thermodynamic equilibrium to the hydrogen under the conditions existing in the reaction zone. The equilibrium concentration of methane corresponding to the hydrogen concentration at reaction zone conditions may be determined by calculation based on the thermodynamic data published by the Carnegie Press for American Petroleum Institute Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds."

It has been found that, if the ratio of equilibrium methane concentration to the actual methane concentration in the reaction zone is maintained above about 1.7 times the thermodynamic equilibrium ratio, the formation of coke may be suppressed or controlled. This operation may be effected by controlling the amount of hydrogen added to the feed or by varying the amount of hydrogen with respect to the feed. In short, either increasing or decreasing the hydrogen or increasing or decreasing the feed aromatic hydrocarbon may allow the formation of carbon in the reaction zone to be controlled.

To illustrate the present invention a number of runs were conducted with the same sulfur dioxide kerosene extract, employed in previous runs, wherein the ratio was varied in accordance with the present invention. These operations are summarized in the following table:

Table I

Run Period, Hours	14–26	26–38	38–50	50–62
Reactor Temperature, ° F	1,290	1,290	1,295	1,295
Reactor Pressure, p.s.i.g	600	600	600	600
Charge Gas:				
S.c.f./bbl. Feed	11,250	11,510	10,330	10,090
H_2, Mol Percent	76.1	77.5	76.4	76.1
Residue Gas:				
Specific Gravity (Referred to Air)	0.428	0.430	0.460	0.465
H_2, Mol Percent	43.4	43.0	38.3	37.5
CH_4, Mol Percent	37.4	37.8	42.1	42.9
Calc. Equil. CH_4, Mol Percent	97.7	95.9	73.8	70.8
Ratio Equil. CH_4/Actual CH_4	2.61	2.54	1.75	1.65

It will be seen that during the series of yield periods, the ratio of the calculated equilibrium concentration of methane to the actual concentration decreased continuously during the yield periods. After 62 hours, the ratio had dropped to a value of 1.65, and the run was terminated by coking.

In another run the concentration of hydrogen and methane in the residue gas were controlled by varying the quantity of the charged gas so that the specific gravity, with reference to air, of the residue gas remained within the limits of 0.43 to 0.45. The results of consecutive yield periods for this run are shown in Table II:

Table II

Run Period, Hours	9–21	21–57	57–69	69–103
Reactor Temperature, ° F	1,315	1,315	1,320	1,325
Reactor Pressure, p.s.i.g	600	600	600	600
Charge Gas:				
S.c.f./bbl. Feed	13,080	11,770	12,440	12,550
H_2, Mol Percent	75.2	76.4	76.3	73.6
Residue Gas:				
Specific Gravity (Referred to Air)	0.436	0.442	0.432	0.446
H_2, Mol Percent	42.1	41.2	42.7	40.5
CH_4, Mol Percent	38.6	39.4	38.1	40.1
Calc. Equil. CH_4, Mol Percent	79.1	75.7	78.8	69.0
Ratio Equil. CH_4/Actual CH_4	2.05	1.92	2.07	1.72

It will be seen from these data that by maintaining the ratio of equlibrium concentration of methane to the actual concentration above about 1.7 that coking is substantially eliminated and further that the operation may be controlled by varying the concentrations of hydrogen and methane in the residue gas.

The present invention is quite advantageous and useful in that coking in hydrodealkylation of aromatic hydrocarbons may be suppressed, controlled or entirely eliminated.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for controlling and suppressing the formation of coke in a thermal dealkylation zone in which an alkylated aromatic hydrocarbon feed is heated in said dealkylation zone in the presence of hydrogen to a temperature within the range between about 1100° and about 1600° F. and at a pressure within the range between about 400 and about 1000 pounds per square inch gauge for a time within the range between about 2 and about 120 seconds in the presence of a fluidized bed of catalytically inert finely divided solids in which a liquid product and a residue gas are produced which comprises the steps of analyzing said residue gas to obtain a signal which is a function of the methane to hydrogen ratio in the residue gas, and employing said signal to vary the ratio of hydrogen and alkylated aromatic hydrocarbon feed in said thermal reaction zone to provide a methane to hydrogen ratio in said residue gas such that the ratio of the thermodynamic equilibrium methane concentration to the actual methane concentration is above about 1.7.

2. A method in accordance with claim 1 in which the amount of hydrogen and alkylated aromatic hydrocarbon feed is varied by varying the amount of hydrogen.

3. A method in accordance with claim 1 in which the amount of hydrogen and alkylated aromatic hydrocarbon feed is varied by varying the amount of alkylated aromatic hydrocarbon.

4. A method for controlling and suppressing the formation of coke in a thermal dealkylation zone in which an alkylated aromatic hydrocarbon feed is heated in said dealkylation zone in the presence of hydrogen to a temperature within the range between about 1100° and about 1600° F. and at a pressure within the range between about 400 and about 1000 pounds per square inch gauge for a time within the range between about 2 and about 120 seconds in the presence of a fluidized bed of catalytically inert finely divided solids in which a liquid product and a residue gas are produced which comprises the steps of flowing said residue gas through a sensing zone to obtain a signal which is a function of the methane to hydro-

gen ratio in the residue gas, and employing said signal to vary the ratio of hydrogen and alkylated aromatic hydrocarbon feed in said thermal reaction zone to provide a methane to hydrogen ratio in said residue gas such that the ratio of the thermodynamic equilibrium methane concentration to the actual methane concentration is above about 1.7.

5. A method in accordance with claim 4 in which the alkylated aromatic hydrocarbon boils within the range from about 200° to about 750° F.

6. A method in accordance with claim 4 in which the amount of hydrogen and alkylated aromatic hydrocarbon feed is varied by varying the amount of hydrogen.

7. A method in accordance with claim 4 in which the amount of hydrogen and alkylated aromatic hydrocarbon feed is varied by varying the amount of alkylated aromatic hydrocarbon.

8. A method in accordance with claim 4 in which the hydrogen is present in an amount within the range of about 6,000 to about 12,000 standard cubic feet per barrel of aromatic hydrocarbon feed.

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