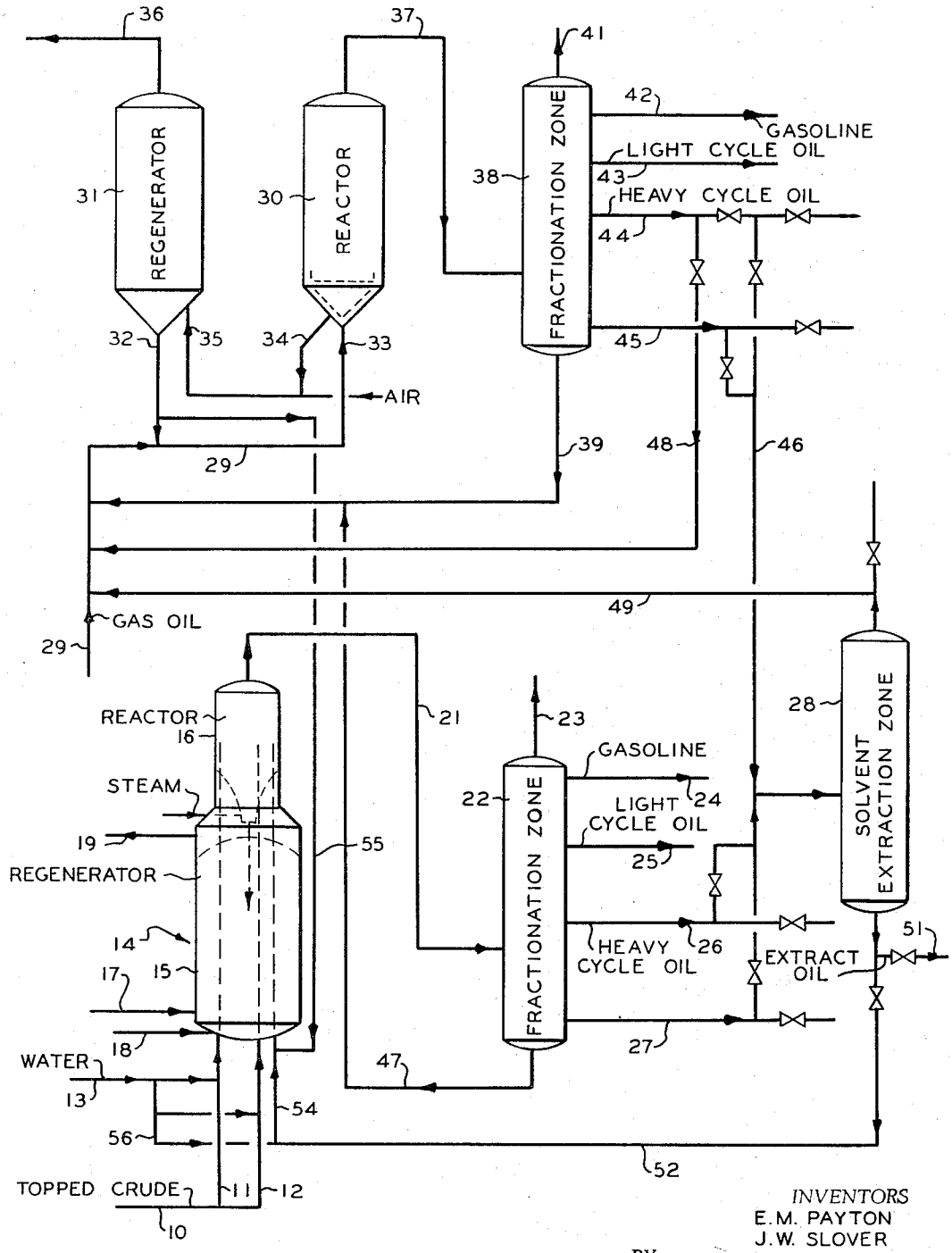
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CATALYTIC CRACKING OF RESIDUUM OILS CONTAINING METAL CONTAMINANTS IN SEVERAL STAGES

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CATALYTIC CRACKING OF RESIDUUM OILS CONTAINING METAL CONTAMINANTS IN SEVERAL STAGES

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This invention relates to catalytic conversion of reactant materials such as hydrocarbons. In one aspect it relates to a method and means for catalytic conversion of hydrocarbons of differing properties at different conditions in a unitary process and apparatus. In one of its more specific aspects it relates to a method and means for the simultaneous and separate catalytic cracking of a hydrocarbon residuum such as topped crude and an aromatic hydrocarbon such as the extract obtained by solvent extraction of the cycle oils resulting from such cracking operation.

It is known to crack hydrocarbon fluids catalytically to increase the quantity and quality of the gasoline or motor fuel product. In such operations a refractory heavy product is produced, for which there is little demand, and therefore this heavy product is usually returned to the cracking operation. It has been proposed to solvent extract this heavy recycle oil so as to remove therefrom aromatic hydrocarbons which are carbon formers and gas formers and to recycle the raffinate from this solvent extraction step to the cracking operation. It has also been proposed to employ two or more catalytic cracking zones, wherein feed stocks containing different concentrations of contaminating metals are separately cracked, to solvent extract the heavier oil from the cracking zone that treats the feed stock containing the least amount of contaminants, to pass the raffinate to the cracking zone wherein the feed stock contains a greater amount of contaminants and to pass the extract oil to a carbon black process. Such process increases the aromatic or extract oil production. The extract from the solvent extraction step constitutes a preferred feed stock for the manufacture of carbon black by the furnace process and a considerable quantity of such extract is consumed in the carbon black process.

In the catalytic cracking of hydrocarbons wherein more than one catalytic cracking zone is employed, it is usually considered desirable to crack residual hydrocarbons, such as topped crude, pitch, and/or other hydrocarbon fluids containing relatively large amounts of metal compound contaminants or other coke- and gas-forming components, in a reaction zone employing catalyst which has been discarded from a catalytic cracking zone wherein distillate hydrocarbons, such as gas oils and recycle oils from the catalytic cracking process which contain relatively small amounts of metal compound contaminants or coke- and gas-forming components, are contacted with a fresh or relatively little-used catalyst. The distillate hydrocarbons are generally more refractory than the residual hydrocarbons and therefore these distillate hydrocarbons are usually catalytically cracked at a higher temperature than are the residual hydrocarbons. The raffinate from the solvent extraction step is usually added as a recycle stream to the catalytic cracking zone wherein distillates are cracked.

The solvent extraction of the heavy cycle oils in the catalytic cracking of hydrocarbons has resulted in the production of extract stocks which are sometimes in excess of the requirements of the carbon black process; however, solvent extracting the cycle oils has so improved these cycle oils in the form of raffinate for the catalytic cracking process that the solvent extraction of these cycle

oils is continued even though an excess of extraction has resulted. The excess of extract oil has been added to the catalytic cracking zone wherein distillates are cracked because the extract is quite refractory and requires cracking temperatures higher than those that are tolerated by the residual oils that are cracked in the cracking zone utilizing the used catalyst. When extract oils are added to the distillate oils in the clean catalyst cracking zone, it is necessary to increase the cracking temperature and thus operate at a compromise temperature between the optimum cracking temperature for the distillate oils and the optimum cracking temperature for the extract oils. In this operation the cycle oils will contain an abnormally large concentration of aromatics.

It is an object of this invention to provide a method for cracking an extract oil in a catalytic cracking process such that the distillate oil charge, the residual oil charge, and the extract oil charge can each be catalytically cracked at its optimum cracking temperature. Another object of this invention is to provide a method for the economic disposal of excess extract oils. Still another object of this invention is to provide a method for cracking an extract oil in a catalytic cracking process so as to provide a minimum concentration of aromatic components in the cycle oils removed from the distillate oil cracking zone. Other and further objects and advantages of the invention will be apparent to one skilled in the art upon study of this disclosure including the drawing and the detailed description of the invention.

The drawing is a diagrammatic flow plan of a preferred embodiment of the invention.

According to the method of the invention, the extract oil is contacted with catalyst in a separate riser in the residual oil cracking zone at a catalyst-to-oil ratio sufficient to crack the extract oil at optimum cracking temperature which is considerably higher than that of the residual oil. The extract oil can be catalytically cracked in a separate riser in the distillate oil cracking zone; however, this is less preferred because of the inherent increase in concentration of aromatic components in the cycle oils removed from this catalytic cracking zone. It is a feature of the invention that make-up catalyst passed from the distillate oil cracking zone to the residual oil cracking zone can be employed as the catalyst for cracking the extract oil and thus the extract oil can be cracked with clean catalyst in the dirty catalyst cracking zone. The residual oils are usually catalytically cracked at a temperature of about 870–940° F. and the distillate oils, being more refractory, are usually catalytically cracked at a temperature of about 890–980° F. The extract oils being considerably more refractory than the other charge stocks are advantageously catalytically cracked at a temperature of about 950–1050° F. The addition of liquid water to the extract oil prior to contacting the oil with hot catalyst aids in conversion of the extract oil. The water addition permits an increase in the catalyst-to-oil ratio.

Referring now to the drawing, a residual oil such as topped crude enters the system via conduit **10** and then is passed into risers **11** and **12** along with liquid water from conduit **13**. The mixture of topped crude and water then passes into catalytic cracker **14** which is composed of a regeneration chamber **15** and a superimposed reactor **16**. This can be referred to as an over-and-under catalytic cracker. The risers **11** and **12** terminate in the reactor **16** above the level of a fluidized bed of catalyst contained therein. A disengaging and stripping section in the lower portion of reactor **16** passes used catalyst from the reactor section downwardly into the regenerator section **15**. Air is admitted to the lower portion of regenerator **15** via conduit **17** and a fluidizing gas is admitted to the bottom portion of regenerator **15** via conduit **18**. The stream of

topped crude entrains catalyst from the regenerator **15** and a mixture of topped crude and catalyst passes upwardly through the risers and is discharged into the reactor section **16**. Combustion gases resulting from regenerating catalyst are removed from regenerator **15** via conduit **19**. The vaporized effluent from reactor **16** is removed via conduit **21** and passed to fractionation zone **22** wherein the effluent products are separated into fractions having different boiling ranges from whence C_4 and lighter materials are removed via conduit **23**, a gasoline cut is removed via conduit **24** and light cycle oil is removed via conduit **25** to form these various products of the process. Heavy cycle oil removed via conduit **26** and decant oil removed via conduit **27** are passed to a solvent extraction plant **28**.

A second hydrocarbon stream comprising a distillate such as gas oil is charged to a second catalytic cracker **30** via conduit **29**. Reactor **30** with its attendant regenerator **31** is illustrated as a side-by-side catalytic cracker as distinguished from the over-and-under catalytic cracker **14**. Regenerated catalyst from regenerator **31** is passed via conduit **32** into conduit **29** so that a mixture of oil and catalyst passes upwardly through riser **33** into reactor **30** wherein a fluidized bed of solid catalyst is maintained. Catalyst is removed from reactor **30** via conduit **34** and is passed along with a conveying stream of air through conduit **35** into regenerator **31**. Combustion gases are removed from regenerator **31** via conduit **36**. Vaporized effluent passes from reactor **30** via conduit **37** to a second fractionation zone **38**. C_4 and lighter hydrocarbons removed via conduit **41**, a gasoline fraction removed via conduit **42** and a light cycle oil removed via conduit **43** are recovered as products of the process. Heavy cycle oil removed via conduit **44** and decant oil removed via conduit **45** are passed via conduit **46** to the solvent extraction zone **28** along with the oil in conduit **27**.

A slurry of catalyst fines and fractionator tower bottoms from fractionation zone **38** is passed via conduit **39** along with a similar slurry of catalyst fines and fractionator tower bottoms from fractionator zone **22** in conduit **47** to conduit **29** as a portion of the feed to catalytic cracker reactor **30**. If desired, a portion of the heavy cycle oil in conduit **44** can be passed via conduit **48** to conduit **29**. The raffinate from solvent extraction zone **28** is passed via conduit **49** to conduit **29**.

Extract oil from solvent extraction zone **28** is removed via conduit **51**. Excess extract oil over that removed as product is passed via conduit **52** to riser **54** in over-and-under catalytic cracker **14**. Hot regenerated catalyst from regenerator **31** is passed via conduit **55** and admixed with the extract oil and steam in riser **54**. Liquid water is passed via conduit **13** and conduit **56** into contact with the extract oil in conduit **52** before it is contacted with catalyst in riser **54**.

Conventional cracking catalysts such as synthetic or natural clays, bauxite, brucite, silica-alumina, and the like can be used in the practice of the invention. Conventional reaction conditions of temperature, pressure, space velocity and the like are applicable in the practice of the invention.

The following example may be helpful in attaining a clear understanding of the invention but should not be construed as limiting the claims unduly.

EXAMPLE

Topped crude and extract oil were cracked separately and as a mixture in an over-and-under catalytic cracker such as cracker **14** of the drawing. The data in the following Table I compare representative runs wherein Run 1 shows conditions for a mixture of extract and topped crude passed to all of the risers, i.e., risers **11**, **12** and **54**; and Run 2 shows conditions for topped crude in risers **11** and **12** and extract in riser **54**.

In the following tables the following abbreviations are employed:

BMCI=Bureau of Mines Correlation Index
b./d.=Barrels per day
b./hr.=Barrels per hour
lb./hr.=Pounds per hour
LV percent=Liquid volume percent
Wt. ratio=Weight ratio

Table I

COMPARISON OF CRACKING EXTRACT SEPARATELY AND MIXED WITH TOPPED CRUDE

	Run 1	Run 2	
	Risers 11, 12 and 54	Risers 11 and 12	Riser 54
Extract, b/d	2,600		2,600
API at 60° F			10
BMCI			95
Temp. of Feed, ° F	365		100
H_2O added, b./hr	*32		12
Steam, lb./hr	*11,000		5,000
Catalyst/oil wt. ratio	*13:1		23:1
Riser Outlet, ° F	960		990
Conversion, LV percent	*57		41
Topped Crude, b./d	20,000	20,000	
API at 60° F		22	
Temp. of Feed, ° F	365	400	
H_2O added, b./hr	*32	20	
Steam, lb /hr	*11,000	6,000	
Catalyst/oil wt. ratio	*13:1	11.5:1	
Riser Outlet, ° F	960	935	
Conversion, LV percent	*57	59	

*Value for the mixture of extract and topped crude.

The production of gasoline and coke is compared with total charge and conversion values in the following Table II.

Table II

PRODUCTION

	Run 1	Run 2	Run 3
Topped Crude, b./d	20,000	20,000	21,915
Extract, b./d	2,600	2,600	2,845
Total Charge, b./d	22,600	22,600	24,760
Conversion, b./d	12,860	12,860	14,090
Conversion, LV percent	57	57	57
Gasoline, b./d	9,130	9,432	10,330
Coke, lb./hr.	38,100	34,770	38,100

Comparison of Runs 1 and 2 shows that by operating according to the invention (Run 2) gasoline production is increased 300 barrels per day and coke production is reduced about 80,000 pounds per day at the same conversion level. The unit is limited to producing 38,100 pounds of coke per hour because this is the maximum amount of coke that can be burned in the regeneration step without raising the temperature of the regenerated catalyst to a value higher than can be tolerated in the cracking operation. Thus it can be seen that practice of the invention as in Run 2 reduces coke production so that the total charge to the unit can be increased as shown in Run 3 so that gasoline production is increased to 10,330 barrels per day at maximum coke production. This means that gasoline production can be increased by 1200 barrels per day in this unit by practice of the invention.

That which is claimed is:

1. In the catalytic cracking of hydrocarbons wherein residuum containing a relatively large amount of metal contaminants is charged to a first catalytic cracking zone admixed with hot, regenerated, dirty catalyst at a catalyst-to-oil ratio sufficient to raise the temperature of the residuum charge to about 870 to 940° F., distillate oils containing a relatively small amount of metal contaminants are charged to a second catalytic cracking zone admixed with hot, regenerated, clean catalyst at a catalyst-to-oil ratio sufficient to raise the temperature of the dis-

tillate oils to about 890 to 980° F., cycle oils are solvent extracted, and the raffinate from the solvent extraction step are charged to the second catalytic cracking zone as a portion of the distillate oil charge, the improvement comprising charging extract from said solvent extraction step to said first catalytic cracking zone in a separate zone within said first zone admixed with hot, regenerated catalyst at a catalyst-to-oil ratio sufficient to raise the temperature of the extract charge to about 950 to 1050° F.

2. The process of claim 1 wherein liquid water in the amount of about 1 to 10 pounds of water per barrel of extract is added to the extract charge before the catalyst is admixed with the extract.

3. The process of claim 1 wherein the catalyst admixed with the extract oil is clean catalyst from said second cracking zone.

4. The process of claim 1 wherein the catalyst admixed with the extract oil is dirty catalyst from said first cracking zone.

5. In the catalytic cracking of hydrocarbons wherein the hydrocarbon charge to a reaction zone is admixed with hot, regenerated catalyst at a catalyst-to-oil ratio sufficient to raise the temperature of the hydrocarbon charge to a predetermined level, the catalyst-to-oil ratio of the residuum charge in a first reaction zone is sufficient to raise the residuum charge to a temperature in the range of about 870 to 940° F., and the catalyst-to-oil ratio of the distillate charge in a second reaction zone is sufficient to raise the distillate charge to a temperature in

the range of about 890 to 980° F., the improvement comprising charging an extract from a solvent extraction step and hot, regenerated catalyst to a third reaction zone within said first reaction zone at a catalyst-to-oil ratio sufficient to raise the temperature of the extract charge in said third reaction zone to the range of about 950 to 1050° F.

6. In the catalytic cracking of hydrocarbons wherein residuum is charged to a first catalytic cracking zone at a temperature of about 935° F., distillate oils are charged to a second catalytic cracking zone at a temperature of about 950° F., cycle oils are solvent extracted and the raffinate from the solvent extraction step is charged to said second catalytic cracking zone at a temperature of about 950° F., the improvement comprising charging extract from said solvent extraction step to a third catalytic cracking zone within said first zone at a temperature of about 990° F.

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