

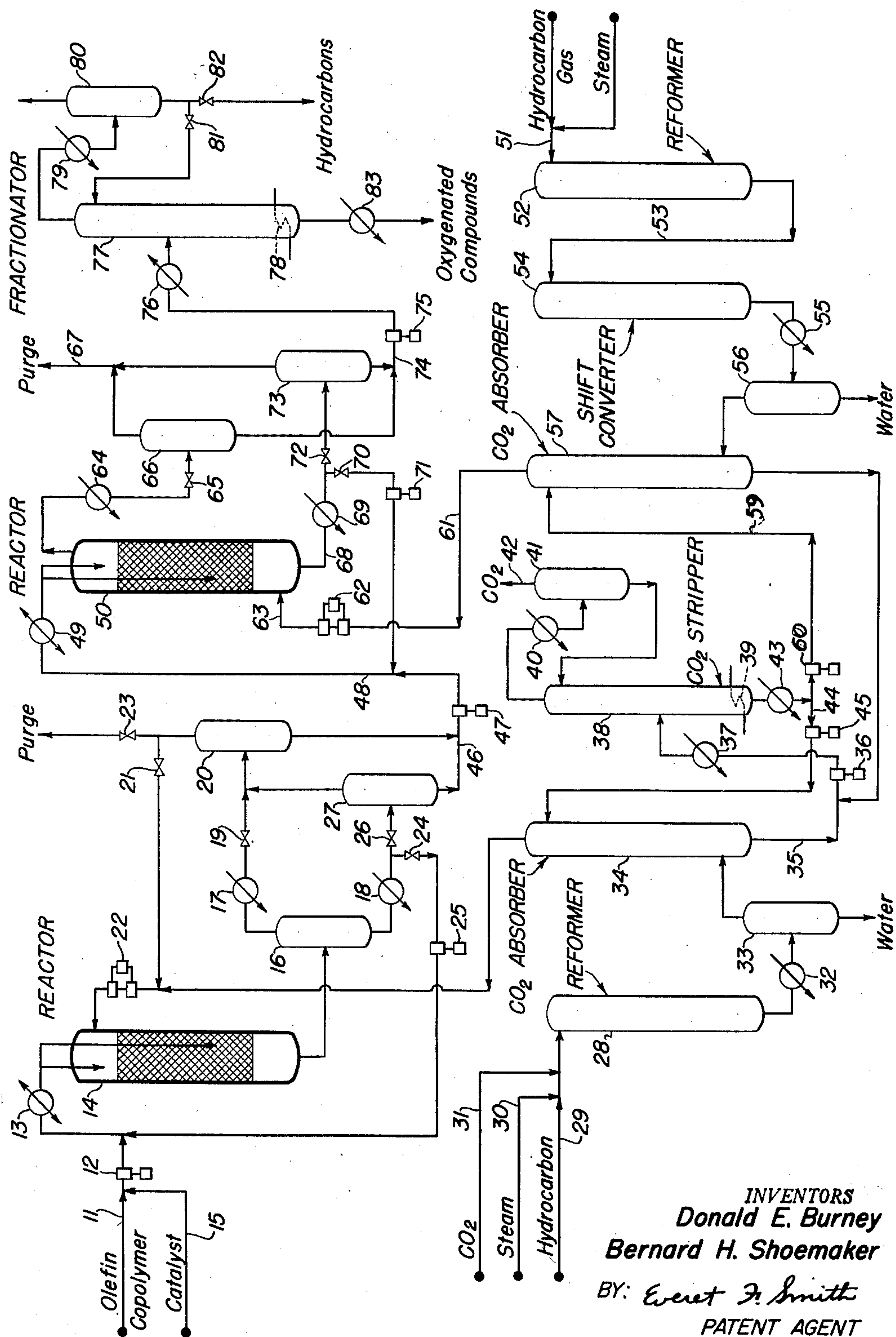
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PREPARATION OF IMPROVED MOTOR FUEL

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PREPARATION OF IMPROVED MOTOR FUEL

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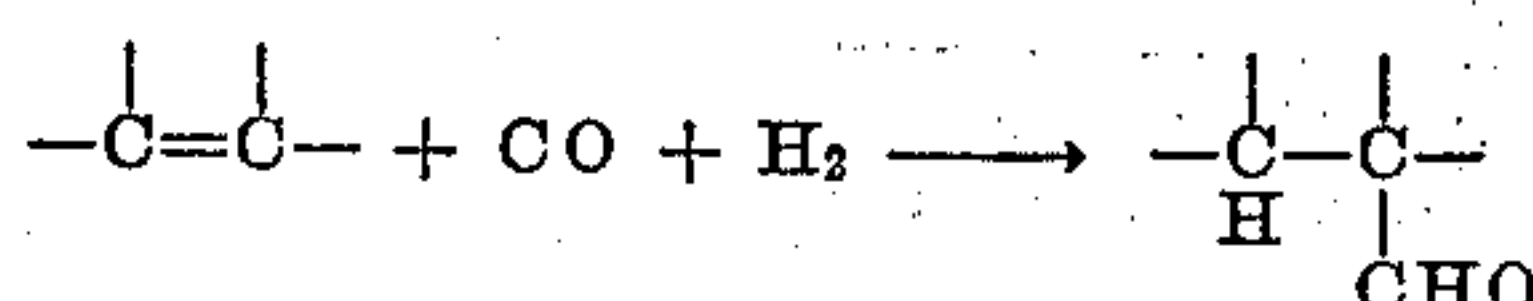
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Our invention relates to the preparation of superior motor fuels from olefin copolymers. More particularly, it relates to a method for reacting secondary olefin-tertiary olefin copolymers with carbon monoxide and hydrogen and obtaining thereby a sensitive motor fuel of high performance number.

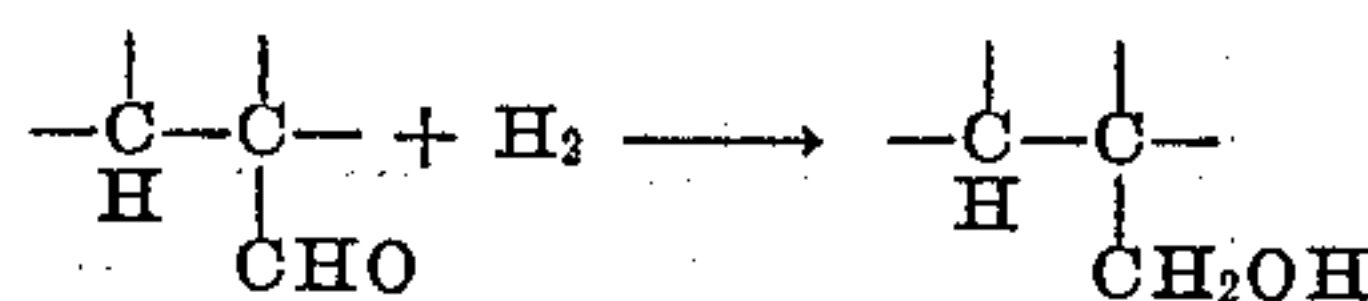
The determination and specification of gasoline quality is a problem that has occupied the attention of automotive engineers for many years. At present, one particular phase of gasoline quality is expressed in terms of "octane numbers," or preferably in terms of "performance numbers." On octane number is an anti-knock rating of a gasoline in terms of the percentage of isooctane (2,2,4-trimethylpentane) in a binary mixture of isooctane and n-heptane which exhibits knocking at the same compression ratio as the gasoline under specified test conditions. A performance number, on the other hand, is the knock-limited power output obtainable from a given gasoline under the test conditions, expressed in terms of percentage of the power obtainable with pure isooctane under the same test conditions. (See Brooks, "Development of Reference Fuel Scales for Knock Rating," S. A. E. Journal, 54, 394-403, August 1946.) Performance numbers are a superior index of gasoline quality, since unlike octane numbers, they do not suffer a discontinuity at the 100 level. They may be determined by a variety of test methods, of which the two most commonly used are the ASTM-CFR Motor method and the CFR Research method, commonly designated "ASTM Motor" and "CFR Research," respectively. These two methods do not ordinarily give the same performance numbers for a given gasoline; in fact, the difference between the two ratings for a given gasoline is a further measure of its quality, called the "sensitivity" of the gasoline, which is defined as the CFR Research rating minus the ASTM Motor rating. In general, it has been found that of two gasolines having the same ASTM Motor rating, the one having the higher sensitivity will give the better road performance. Sensitive fuels are particularly well adapted to use in aircraft engines, especially fighter planes, where their superior response to large power demands is a distinct advantage.

Our invention makes use of the so-called "Oxo" reaction wherein an olefin is converted first into an aldehyde by reaction with carbon monoxide and hydrogen at elevated temperature and pressure in the presence of an iron or cobalt catalyst,

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and the aldehyde is subsequently hydrogenated by conventional methods to the corresponding alcohol,



Our invention is based on the discovery that carbon monoxide and hydrogen react only partially under "Oxo" process conditions with the gasoline-boiling-range olefinic products resulting from the copolymerization of secondary olefins with tertiary olefins, leaving unaffected an olefin fraction which, on being hydrogenated, is converted into a saturated hydrocarbon mixture of high performance number and high sensitivity.

One object of our invention is to provide a convenient means for segregating olefin copolymers into useful fractions. Another object of our invention is to separate a sensitive motor fuel of high performance number from secondary olefin-tertiary olefin copolymers. Other objects of our invention, and its advantages over the prior art, will be apparent from the following description and examples.

Numerous methods have been devised for the polymerization and copolymerization of olefins to produce higher-boiling materials useful primarily as ingredients of high quality gasolines. Various charging stocks have been utilized, comprising a mixture of the normally gaseous olefins and inert materials, such as paraffin hydrocarbons. In general, the processes employ acidic catalysts, such as sulfuric acid, phosphoric acid, or hydrogen fluoride; potentially acidic catalysts such as copper pyrophosphate or boron fluoride; or solid catalysts such as silica-alumina or acid-treated bentonite. Hot sulfuric acid (140-194° F.), for example, absorbs isobutylene and n-butylene from mixtures of isobutylene, n-butylenes, and inert materials, and produces a primarily dimeric product containing substantially all of the isomeric trimethylpentenes and dimethylhexenes.

In an especially successful and convenient polymerization process, secondary butylenes and isobutylene are polymerized by passage over a solid granular catalyst, comprising phosphoric acid absorbed on clay or other inert material, at 350-500° F. and around 40 atmospheres. Under these conditions, when the charge stream contains 30% of secondary butylenes and 15% of

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isobutylene, approximately 67% of the olefins are converted into a product, of which 85% is dimer and 15% is trimer. Fractional distillation of the crude product yields a dimer fraction having properties and composition as in the following illustrative example:

n-Butylene-isobutylene codimer properties and composition

Mean molecular weight	112.2
Specific gravity, 60/60° F.	0.735
Refractive index, n_D^{20}	1.4200
True boiling range, °F.	212-240
ASTM distillation, °F:	
Initial	210
10%	216
50%	230
90%	231
End	252
Freezing point, °F.	Below -76
Flash point (Tag), °F.	32
Color (Saybolt)	30
Olefin content, percent	Over 99
Total isooctene content, percent	Over 98
Distribution of isooctenes, percent by weight:	
2,2,3-trimethylpentenes	21
2,2,4-trimethylpentenes	10
2,3,3-trimethylpentenes	11
2,3,4-trimethylpentenes	47
Dimethylhexenes	10

By means of our process, we are able to produce sensitive motor fuels of high performance number from virtually any secondary olefin-tertiary olefin copolymer containing a substantial proportion of components boiling between about 100 and 400° F. at one atmosphere, the usual gasoline boiling range. Especially suited for our process are copolymers of mixtures containing at least one olefin from the group comprising propylene, secondary butylenes, and secondary amylenes, and at least one olefin from the group comprising isobutylene, 2-methyl-1-butene, and 2-methyl-2-butene.

In carrying out our invention, we selectively carbonylate a secondary olefin-tertiary olefin copolymer, such as the *n*-butylene-isobutylene codimer described above, by contacting it with a mixture of hydrogen and carbon monoxide having a molar ratio between about 0.5:1 and 5:1 at a temperature between about 200 and 500° F., a pressure between about 50 and 300 atmospheres, and a liquid space velocity between about 0.05 and 10 per hour, in the presence of a catalyst comprising cobalt and/or iron. We prefer to carry out the reaction between about 275 and 425° F., optimally between 375 and 425° F., at a pressure around 200 atmospheres and with a mixture of hydrogen and carbon monoxide having a molar ratio between about 1:1 and 3:1. Under these conditions, between 10 and 60% of *n*-butylene-isobutylene codimer is converted into nonyl aldehydes and alcohols in a reaction time between about 30 and 120 minutes.

Catalysts comprising cobalt and/or iron are suitable for the selective carbonylation reaction of our invention. The catalyst may be used in the pure, finely divided form; or it may be supported on powdered or pelleted inert carriers, such as silica, pumice, or kieselguhr; or it may be added to the feed mixture in the form of metal carbonyls, or oil-soluble salts of organic acids, such as the naphthenates, stearates, laurates,

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benzoates, phthalates, and the like. Various promoters, such as thoria, magnesia, and the like, may be combined with the catalytic material, and various non-carbonyl-forming metals, such as silver, copper, and the like, may be incorporated in the catalyst to repress the formation of iron or cobalt carbonyls, which tend to dissolve in the reaction mixture, and to be carried out of the reactor with the reaction product. The use of hydrogen in greater than equimolar ratio, based on carbon monoxide, is also advantageous in retarding carbonyl formation. Operation at the higher temperatures within the preferred range also tends to minimize the loss of catalyst from the reactor. For example, we have found that a reaction mixture, after reaching equilibrium with an equimolar mixture of hydrogen and carbon monoxide at 3,000 lb./in.² and 265° F., contains up to about 30 pounds of dissolved cobalt per thousand gallons; at 330° F. it contains up to about 16 pounds per thousand gallons; and at 400° F. it contains less than one pound per thousand gallons.

The reaction may be carried out either batch-wise or in flow equipment. In the former case, the catalyst is most conveniently added to the charging stock in the form of a slurry. In the latter case, the catalyst may satisfactorily be used as a fixed bed; or alternatively it may be added to the charging stock in the form of the metal carbonyls or oil-soluble organic-acid salts, in which case the fixed bed may be used or omitted as desired. Cooling of the reactor may conveniently be accomplished by recycling either the liquid product or the gaseous effluent. The hydrogen-carbon monoxide mixture is preferably supplied to the flow equipment at a space velocity between about 20 and 1000 volumes of gas, measured at standard temperature and pressure, per volume of catalyst zone per hour.

In the carbonylation stage, a portion of the olefinic charging stock is converted into aldehydes and alcohols. The remainder of the olefinic charge is resistant to carbonylation; and may be converted by hydrogenation into a sensitive gasoline of high performance number. Such hydrogenation may be effected in part during the carbonylation reaction if the carbonylation is carried out under severe conditions. The hydrogenation may then be completed by subjecting the crude product to the action of hydrogen in the presence of a hydrogenation catalyst such as nickel, iron, copper, copper chromite, and the like, or mixtures thereof, suitably at temperatures between about 150 and 700° F. and at pressures above about 50 atmospheres. First, however, it is desirable to remove substantially all carbon monoxide from the carbonylation product by suitable means, such as by purging with hydrogen or an inert gas, or by washing the liquid successively with an acid and with water.

If desired, the non-carbonylated olefins may be hydrogenated selectively to paraffins without simultaneous hydrogenation of the aldehydes, in the presence of nickel, iron, or copper catalysts, or the like, at temperatures between about 100 and 150° F. and at pressures below about 75 atmospheres. After the hydrogenation step, the gasoline and by-product fractions may be separated conveniently by conventional means, such as by extraction with a selective solvent, by extractive distillation, by azeotropic distillation, or by fractional distillation.

Alternatively, the aldehydes may be selectively hydrogenated in the presence of a cobalt catalyst, suitably at a temperature between about 350 and

600° F., a pressure between about 500 and 1500 pounds per square inch, and a liquid space velocity between about 0.2 and 2.0 per hour, as disclosed in the copending Burney-Cervený joint application, Serial No. 788,847, filed November 29, 1947, now forfeited in favor of a continuation-in-part thereof, Serial No. 223,124, filed April 26, 1951; and after separation of the resulting alcohols, suitably by distillation, the olefins left thereby may be converted into a high quality motor fuel by hydrogenation in the presence of a conventional hydrogenation catalyst, such as nickel. Mild conditions are suitable; for example, temperatures between about 75 and 150° F. and pressures below about 25 atmospheres may be used satisfactorily.

As a further alternative, prior to the hydrogenation step, the carbonylated and non-carbonylated groups of compounds may be separated by suitable means, such as by extraction with a selective solvent, by extractive distillation, by azeotropic distillation, or by fractional distillation, after which the non-carbonylated materials may be converted into a superior motor fuel by hydrogenation, suitably under the mild conditions defined above.

The attached flow sheet illustrates a continuous process for carrying out our invention. Olefin copolymer, supplied through line 11, is injected by pump 12 through heat exchanger 13 into reactor 14, which is maintained at a pressure between about 100 and 300 atmospheres, preferably about 200 atmospheres, and a temperature between about 200 and 500° F., preferably between about 375 and 425° F. The rate of injection of copolymer is suitably between about 0.2 and 10 volumes per hour per unit volume of reaction zone, and preferably between about 0.5 and 1 per hour. The reactor is packed with a suitable catalyst, such as metallic cobalt supported on an inert siliceous material, arranged in such manner that efficient contact is obtained between the liquid hydrocarbon and the reactant gases. Makeup catalyst, suitably metal carbonyls, such as cobalt or iron carbonyl, or oil-soluble organic-acid salts, such as iron or cobalt stearates or naphthenates, may be added through line 15 to the copolymer stream in line 11, in order to compensate for any loss of catalyst from the reactor through carbonyl formation therein, or through mechanical losses. Alternatively, solid catalyst may be omitted from the reactor altogether, and the total catalyst requirements may be supplied with the charging stock in the form of metal carbonyls (suitably between about 0.1 and 2% by weight) or metal salts of organic acids (suitably between about 0.1 and 10% by weight). The reacted liquid stream and the residual gas stream are withdrawn from the base of the reactor to high-pressure separator 16. Here, the stream is divided into liquid-phase and gas-phase streams, which flow separately through coolers 17 and 18 respectively. The cooled gas stream from cooler 17 is expanded through valve 19 into low-pressure separator 20, where condensed liquids are removed. The gas stream emerging from separator 20 is again divided; part of it flowing through valve 21 to compressor 22, from which it is recycled to reactor 14, and the remainder being purged through valve 23 as required to prevent the build-up of inerts in the gas stream. The liquid from cooler 18 is divided into two streams. One stream is recycled through valve 24, pump 25, and heat exchanger 13 to reactor 14 for the purpose of controlling the temperature therein during the ex-

othermic reaction between the copolymer stream, hydrogen, and carbon monoxide. The rate of recycle may be adjusted to maintain the desired temperature, the cooling liquid being introduced at the top of the reactor or at such points within it as may be required to control localized heating. The other liquid stream from cooler 18 flows through blow-down valve 26 to low-pressure separator 27, where dissolved gases are flashed off into separator 20.

The mixture of hydrogen and carbon monoxide required for reactor 14 is supplied from reformer furnace 28, wherein a hydrocarbon gas, such as natural gas or a refinery gas, introduced through line 29, is reformed with steam, introduced through line 30, to produce hydrogen, carbon monoxide, and carbon dioxide. Carbon dioxide is optionally introduced through line 31 into the feed gas stream to increase the ratio of carbon monoxide to hydrogen in the product gas stream. The reformer product gases flow through cooler 32 into separator 33, where water is withdrawn, and from the separator into absorber 34, where the carbon dioxide is scrubbed out with aqueous monoethanolamine. The resulting carbon dioxide-monoethanolamine solution passes through line 35, pump 36, and heater 37 into the top of stripper 38, where carbon dioxide is removed by reboiler 39. The carbon dioxide stream emerges overhead through cooler 40 into separator 41, from which condensed liquids are refluxed to the top of stripper 38. The carbon dioxide from separator 41 is withdrawn through line 42, and may be recycled to reformer 28 through line 31, if desired, to increase the ratio of carbon monoxide to hydrogen in the reformer product gas. Regenerated monoethanolamine solution flows from the bottom of stripper 38, and is recirculated through cooler 43, line 44, and pump 45 to the top of absorber 34. The mixture of gases emerging from absorber 34 is in the ratio of about 0.5 to 5 volumes of hydrogen per volume of carbon monoxide, and is preferably in the range of about 1:1 to 3:1. This mixture flows into compressor 22, by which it is injected into reactor 14, suitably at the rate of about 0.5 to 20 volumes, measured at standard temperature and pressure, per volume of reaction zone per hour. The preferred range is from about 1.3 to 2 times the space velocity of the liquid feed.

The liquid streams from separators 20 and 27 are combined in line 46 and transferred by pump 47 through line 48 and heat exchanger 49 into hydrogenation reactor 50. This liquid stream comprises a crude mixture of aldehydes, alcohols, and non-carbonylated olefins, and ordinarily contains minor proportions of the catalyst from the previous stage, either in the form of the metal carbonyl, oil-soluble metal salts, or suspended solids. If desired, the liquid stream may be subjected to additional process steps to remove the catalyst before the liquid is introduced into reactor 50. The liquid stream may suitably be scrubbed with a dilute acid, such as sulfuric acid, and then with water; or it may be treated with hydrogen or other inert gases at elevated temperatures, for example, above about 150° F., in order to destroy metal carbonyls, and the precipitated metal may then be removed by filtration or centrifugation (apparatus not shown). The hydrogenation reactor 50 is packed with a suitable hydrogenation catalyst, comprising nickel, iron, copper, or the like, preferably on an inert support. The reaction conditions are adjusted according to the type of catalyst used; with finely

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divided metallic nickel catalyst, for example, the preferred pressures are of the order of magnitude of around 60 atmospheres and the temperatures are between about 150 and 300° F., in order to hydrogenate substantially all of the aldehydes to alcohols, and to produce saturated compounds from the unreacted olefins.

Hydrogen for reactor 50 is conveniently prepared by reforming a hydrocarbon gas with steam to produce a mixture of hydrogen and carbon monoxide, then subjecting the mixture to the water-gas shift reaction to convert the carbon monoxide to carbon dioxide, and finally scrubbing out the carbon dioxide, leaving a purified hydrogen stream. A hydrocarbon gas and steam are introduced through line 51 into reformer 52, where they are converted by the action of a ceria-promoted nickel catalyst at 1800° F. into a mixture of hydrogen, carbon monoxide, carbon dioxide, and unreacted steam. The gases are then introduced through line 53 into shift converter 54. Therein, the gases are contacted with a suitable catalyst, such as iron, at a temperature between about 500 and 1000° F., whereby substantially all of the carbon monoxide is converted into carbon dioxide. The treated gases emerge through cooler 55 into separator 56, from which water is withdrawn, and are then introduced into the bottom of absorber 57, where the carbon dioxide is scrubbed out with aqueous monoethanolamine. The carbon dioxide-monoethanolamine solution emerging from the bottom of absorber 57 flows through line 58, pump 36, and heater 37 into stripper 38; and regenerated monoethanolamine solution is supplied from stripper 38 through cooler 43, line 59, and pump 60 to the top of absorber 57.

A purified hydrogen stream emerges overhead from absorber 57 through line 61. If desired, any traces of carbon oxides remaining in the hydrogen may be removed by subjecting it to methanation, under conditions described in the prior art (apparatus not shown). For example, the hydrogen may be passed over a nickel catalyst at a temperature between about 350 and 650° F. The purified hydrogen flows into compressor 62, and after compression is introduced into reactor 50 through line 63. The hydrogen passes upward through the downward-flowing liquid stream, the aldehydes therein being converted thereby into alcohols, and the olefins being converted into the corresponding saturated hydrocarbons. Excess gas is withdrawn at the top of the reactor through cooler 64 and expanded through valve 65 into low-pressure separator 66, from which the gases are withdrawn and purged in part through line 67 to prevent the accumulation of inert constituents, and recycled in part if desired, suitably to reformer 52 (lines not shown). From the bottom of reactor 50, liquid is withdrawn through line 68 into cooler 69. The cooled liquid stream is divided, part of it being recycled through valve 70, pump 71, line 48, and heat exchanger 49 to reactor 50 to assist in maintaining the reaction temperature at the desired level, while the remainder of the stream is reduced in pressure to around one atmosphere through valve 72 and allowed to flow into low-pressure separator 73, where the dissolved gases are flashed off and vented or recycled as desired.

The liquid streams from separators 66 and 73 are combined in line 74 and transferred by pump 75 through heater 76 into fractionating column 77 at an intermediate point. The hydrocarbon constituents are fractionally distilled overhead by

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reboiler 78, and are condensed in cooler 79. The condensate flows into reflux drum 80, from which a portion is refluxed through valve 81 to the top of the column, and the remainder is withdrawn through valve 82 as the sensitive, high performance-number motor-fuel fraction.

The bottoms stream from column 77, comprising alcohols and other oxygenated hydrocarbon derivatives, is withdrawn through cooler 83 and sent to storage or further processing. The mixed alcohols and oxygenated compounds may be used as such; or they may be subjected to further fractionation to isolate substantially pure components; or, if desired, they may be reconverted to olefins by treatment in the vapor phase over alumina at temperatures around 900° F., and the olefins may then be recycled to reactor 14.

It will be noted that reactor 14 is shown with liquid and gas flowing concurrently downward, whereas in reactor 50 the liquid stream flows downward countercurrent to the gas stream. It is intended that either of these flow systems may be used in either reactor. Moreover, a third modification, in which the liquid and gas flow upward in parallel, may also be used in either reactor.

The following specific examples will more clearly illustrate our invention:

EXAMPLE I

A supported catalyst containing 8.1% cobalt was prepared by commingling a solution of cobalt nitrate with 10-20 mesh "Filtros" (bonded silica) and evaporating to dryness, then decomposing the nitrate to the oxide by heating, subsequently charging the material into a stainless-steel reactor having a catalyst zone with a length-to-diameter ratio of 26.6 and finally reducing the cobalt oxide with hydrogen at 700° F. and atmospheric pressure.

Three series of experiments were then carried out by passing n-butylene-isobutylene codimer and an equimolar mixture of hydrogen and carbon monoxide concurrently downward through the reactor at an average pressure around 3,000 pounds per square inch and an average space velocity around 0.45 volume of codimer per volume of catalyst zone per hour. The gas mixture was introduced at a space velocity around 200 volumes of gas, measured at standard temperature and pressure, per volume of catalyst zone per hour. After emerging from the reactor, the effluent liquid was cooled, flashed to atmospheric pressure, and removed from the system.

In each of the experiments, after a quantity of the effluent liquid had been accumulated, it was passed again through the reactor one or more times under similar conditions, without being subjected to intermediate processing steps, in order to determine the effect of longer exposure to the reaction conditions.

The results of the experiments were as follows:

Experiment No. 11

Pass No.	1	2	3	4
Temperature, °F.	412	409	405	402
Liquid sp. vel., hr. ⁻¹	0.41	0.46	0.46	0.44
Product composition, vol. percent:				
Hydrocarbons	82.6	69.8	62.1	54.6
Aldehydes	14.6	17.2	21.5	28.4
Alcohols	0	4.8	8.6	11.9
High-boilers	2.6	1.3	1.8	3.9
Soluble Co in product, lb./1,000 gal.	1.40	0.49	1.30	1.71

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Experiment No. 12

Pass No.	1	2	3	4
Temperature, °F	323	333	324	328
Liquid sp. vel., hr. ⁻¹	0.44	0.41	0.42	0.49
Product composition, vol. percent:				
Hydrocarbons	81.0	61.9	57.0	45.8
Aldehydes	9.8	25.8	30.1	37.6
Alcohols	5.7	2.6	5.4	8.0
High-boilers	0.8	3.1	3.6	4.4
Soluble Co in product, lb./1,000 gal.	4.54	7.00	6.42	9.34

Experiment No. 13

Pass No.	1	2
Temperature, °F	281	275
Liquid sp. vel., hr. ⁻¹	0.42	0.41
Product composition, vol. percent:		
Hydrocarbons	84.9	75.1
Aldehydes	9.3	16.2
Alcohols	2.1	1.6
High-boilers	1.0	2.0
Soluble Co in product, lb./1,000 gal.	12.01	12.67

The hydrocarbon components of the above reaction products were separated by fractional distillation and were subsequently hydrogenated to complete saturation by passage over a nickel catalyst supported on 1/8-inch kieselguhr pellets in contact with hydrogen at 300° F. and one atmosphere. Performance-number determinations were then run on samples of the hydrocarbons, both before and after hydrogenation.

For comparison, a quantity of the codimer charging stock was similarly hydrogenated, and performance numbers were determined on the material before and after hydrogenation.

The results were as follows:

	Performance Number		Sensitivity
	ASTM Motor	CFR Research	
Codimer charging stock	59.4	91.2	31.8
Recovered olefins	59.7	91.5	31.8
Hydrogenated codimer	81.4	97.6	16.2
Hydrogenated recovered olefins	79.1	103.6	24.5

Motor fuels of superior performance number and sensitivity were also prepared by reacting n-butylene-isobutylene codimer with carbon monoxide and hydrogen in various other ways, as described in the following examples, and subsequently hydrogenating the carbonylation-resistant olefins.

EXAMPLE II

Inert, 4-8 mesh Filtros was packed in a reactor zone having a length-to-diameter ratio of 26.6. Two series of experiments were then carried out by passing n-butylene-isobutylene codimer containing cobalt naphthenate in solution downward through the reactor concurrently with an equimolar mixture of hydrogen and carbon monoxide at an average pressure around 2,800 pounds per square inch and an average space velocity around 0.4 volume of codimer per volume of Filtros zone per hour. The gas mixture was introduced at a space velocity around 200 volumes of gas, measured at standard temperature and pressure, per volume of Filtros zone per hour. In each experiment, the effluent liquid was cooled, flashed to atmospheric pressure, and removed from the system; and the accumulated effluent liquid was passed through the reactor three additional times under the same conditions, without intermediate

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processing steps, and without the introduction of any additional quantity of cobalt naphthenate.

The results of the experiments were as follows:

Experiment No. 16

Pass No.	1	2	3	4
Catalyst concentration, lb. Co/1,000 gal.	4.4			
Temperature, °F	394	409	402	415
Liquid sp. vel., hr. ⁻¹	0.46	0.37	0.44	0.39
Product composition, vol. percent:				
Hydrocarbons	79.2	68.1	63.9	58.3
Aldehydes	18.5	20.6	24.3	24.5
Alcohols	0	5.7	6.5	7.7
High-boilers	0.5	1.8	2.1	3.9
Soluble Co in product, lb./1,000 gal.	1.08	0.41	0.47	0.47

Experiment No. 18

Pass No.	1	2	3	4
Catalyst concentration, lb. Co/1,000 gal.	6.9			
Temperature, °F	330	320	332	327
Liquid space velocity, hr. ⁻¹	0.39	0.44	0.49	0.51
Product composition, vol. percent:				
Hydrocarbons				50.7
Aldehydes				33.8
Alcohols				5.5
High-boilers				5.3
Soluble Co in product, lb./1,000 gal.				0.35

EXAMPLE III

n-Butylene-isobutylene codimer containing dissolved cobalt naphthenate was passed upward through a reaction tower, concurrently with an equimolar mixture of hydrogen and carbon monoxide. The effluent liquid was subjected to one or more additional passes through the reactor, without intermediate processing or addition of extra catalyst. The residence time of the liquid within the reactor was approximately 1.7 hours per pass. The results were as follows:

Experiment No. 25

Pass No.	1	2	3
Catalyst concentration, lb. Co/1,000 gal.	1.66		
Temperature, °F	326	329	327
Pressure, lb./in. ²	3,000	3,000	3,000
Product composition, vol. percent:			
Hydrocarbons	65.4	58.5	59.2
Aldehydes	18.1	21.3	24.7
Alcohols	2.7		
High-boilers	1.6	6.5	9.2

Experiment No.	23	21	24
No. of passes	3	2	3
Catalyst concentration, lb. Co/1,000 gal.	6.6	5.8	1.66
Avg. temperature, °F	402	330	405
Avg. pressure, lb./in. ²	3,000	2,440	2,915
Final product composition, vol. percent:			
Hydrocarbons	33.3	48.4	64.0
Aldehydes	21.9	24.1	23.6
Alcohols	29.2	10.6	6.3
High-boilers	10.3	9.8	2.4

The foregoing examples are submitted only as illustrations of convenient and advantageous methods for carrying out the process of our invention, and are not intended to limit the broad applicability thereof in any way. It is to be distinctly understood that any modifications or equivalents that would ordinarily occur to those skilled in the art are to be considered as lying within the scope of our invention.

In accordance with the foregoing specification, we claim as our invention:

We claim:

1. In a process for producing a superior motor fuel from a secondary olefin-tertiary olefin copolymer, said copolymer containing a substantial

proportion of gasoline-boiling-range components, the steps which comprise contacting said copolymer with carbon monoxide and hydrogen in the presence of a catalyst containing as the active constituent a metal selected from the group consisting of cobalt and iron under conditions of temperature and pressure whereat a portion, but not all, of said gasoline-boiling-range components are converted into oxygenated derivatives, contacting the resulting reaction product with hydrogen under hydrogenating conditions in the presence of a catalyst effective for the hydrogenation of the unconverted portion of said copolymer, whereby the unconverted portion of said gasoline-boiling-range components are converted into a saturated motor fuel of improved sensitivity and performance number, and separating said motor fuel therefrom.

2. The process of claim 1 wherein said copolymer is a copolymer of an olefin mixture comprising a secondary butylene and isobutylene.

3. The process of claim 1 wherein said copolymer is a copolymer of an olefin mixture comprising propylene and isobutylene.

4. The process of claim 1 wherein said copolymer is a copolymer of an olefin mixture comprising a secondary butylene and a tertiary amylene.

5. The process of claim 1 wherein said copolymer is contacted with carbon monoxide and hydrogen in the presence of metallic cobalt.

6. In a process for producing a superior motor fuel from a secondary olefin-tertiary olefin copolymer, said copolymer containing a substantial proportion of gasoline-boiling-range components, the steps which comprise contacting said copolymer with carbon monoxide and hydrogen in the presence of a catalyst containing cobalt as the active constituent under conditions of temperature and pressure whereat a portion, but not all, of said gasoline-boiling-range components are converted into oxygenated derivatives, separating the unconverted portion of said gasoline-boiling-range components from the resulting reaction product, and contacting said unconverted portion with hydrogen under hydrogenating conditions in the presence of a catalyst effective for the hydrogenation thereof, whereby said portion is converted into a saturated motor fuel of improved sensitivity and performance number.

7. In a process for producing a superior motor fuel from a gasoline-boiling-range copolymer of an olefin mixture, said olefin mixture consisting predominantly of a secondary olefin and a tertiary olefin, the steps which comprise contacting said copolymer with carbon monoxide and hydrogen having a ratio between about 0.5 and 5 moles of hydrogen per mole of carbon monoxide in the presence of a cobalt catalyst at a temperature between about 200 and 500° F. and a pressure above about 50 atmospheres, whereby a portion, but not all, of said copolymer is converted into oxygenated derivatives, separating the unconverted portion of said copolymer from the result-

ing reaction product, and contacting said unconverted portion of said copolymer with hydrogen under hydrogenating conditions in the presence of a catalyst effective for the hydrogenation thereof, whereby said portion of said copolymer is converted into a saturated motor fuel of improved sensitivity and performance number.

8. In a process for producing a superior motor fuel from a gasoline-boiling-range copolymer of an olefin mixture, said olefin mixture consisting predominantly of a secondary olefin and a tertiary olefin, the steps which comprise contacting said copolymer with carbon monoxide and hydrogen having a ratio between about 0.5 and 5 moles of hydrogen per mole of carbon monoxide in the presence of a cobalt catalyst at a temperature between about 200 and 500° F. and a pressure above about 50 atmospheres, whereby a portion, but not all, of said copolymer is converted into oxygenated derivatives; contacting the resulting reaction product with hydrogen at a temperature between about 150 and 700° F. and a pressure above about 50 atmospheres in the presence of a catalyst selected from the group consisting of nickel, iron, copper, and copper chromite, and separating a saturated motor fuel of improved sensitivity and performance number therefrom by distillation.

9. A process for producing a superior motor fuel from a n-butylene-isobutylene codimer which comprises contacting said codimer with an approximately equimolar mixture of carbon monoxide and hydrogen in the presence of a cobalt catalyst at a temperature between about 275 and 425° F. and a pressure between about 50 and 300 atmospheres; contacting the resulting product with hydrogen in the presence of a nickel hydrogenation catalyst at a temperature between about 150 and 700° F. and a pressure above about 50 atmospheres; and subsequently fractionally distilling the reaction product and separating therefrom a sensitive motor fuel of improved performance number.

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