ABSTRACT

A method for the removal of dissolved water or water and ice from hydrocarbon liquids such as petroleum refinery fuels or natural gas liquids in a manner which enables the fuels to be readily treated by the coalescence/separation technique while reducing the potential for plugging filters and other equipment with ice crystals. Free water or water/ice is removed from the liquid hydrocarbons by contacting the hydrocarbon feed with a treating agent which has an affinity for water prior to subjecting the mixture to coalescence/separation. The treating agent is preferably a co-solvent for the water and the hydrocarbon such as an alcohol e.g. methanol. The treating agent and water are separated from the hydrocarbon component during the coalescence/separation and recirculated to the feed with the composition of the recycle aqueous phase being controlled to achieve the desired level of water removal to meet relevant product specifications. Consistent with the removal of the water during the coalescence/separation, the water concentration of the recycle loop containing the co-solvent/water blend gradually increases with removal of the water from the feed. This progressive increase in water level can be compensated by controlled addition of pure co-solvent to the recycle coupled with continuous or periodic dumping of excess mixture. Alternatively, the circulating mixture may be subjected to continuous or batch regeneration or disposed of in any other way which is convenient and economical.
SEPARATION OF WATER FROM HYDROCARBONS

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application relates to and claims priority to U.S. Provisional Patent Application No. 60/996,602 filed on Nov. 27, 2007.

FIELD OF THE INVENTION

[0002] This invention relates to a method for the separation of water from hydrocarbons, especially liquid hydrocarbons such as petroleum naphthas, natural gas condensates, petroleum fuels such as gasoline, middle distillates such as road diesel fuel and kerosene, particularly under low temperature conditions. The water removed may be present as such in the hydrocarbons or mixed with other water-miscible materials or contaminants which may be removed simultaneously with the water.

BACKGROUND OF THE INVENTION

[0003] Significant amounts of water become mixed with hydrocarbon streams during production and processing. Petroleum refinery streams, for example, may be treated with water, steam or various aqueous solutions during processing in order to carry out the processing and to meet various quality specifications. Steam stripping, caustic treating and amine treating are frequently used in conventional refinery processing and although much of the water introduced in this way can be removed by simple settling procedures, a certain amount of water remains in the fuel after removal of the bulk of the water. Excess amounts of water frequently adversely affect the properties and quality of hydrocarbon fuels, for example, by creating hazes in fuels which would otherwise be clear, accelerating rust and other forms of corrosion on containers and equipment, and by the formation of ice crystals at low temperatures which may lead to plugging of filters and other equipment, for example, fuel injectors. Water may also contain contaminants such as acids which may lead to accelerated corrosion. It is therefore usually necessary to separate any remaining water from petroleum fuels and other products in order to meet various product specifications; the separation may be carried out at the refinery, at the distribution terminal or at the location of use, for example, the airport.

[0004] Product specifications frequently require relatively low levels of water in order to avoid the problems mentioned above, for example, ASTM D 2709 for diesel fuel oils sets a 0.5% volume maximum limit on water in sediment for diesel fuel oils varying from light distillate fuels for road diesels (1D fuel) up to heavy distillate fuels (4D fuel) for low and medium speed diesels operating at constant speed and load. Similar specifications may be found for other hydrocarbon fuels including motor gasoline and middle distillate products including home heating oil, aviation kerosene and vaporizing oil. Products sold in cold climates are particularly subject to problems arising from the freezing of water and the consequence formation of ice crystals at temperatures below freezing, the problems of product quality control are therefore exacerbated in such climates.

[0005] The production of petroleum hydrocarbons from subterranean formations may also result in hydrocarbon streams which are contaminated by water, either alone or mixed with other contaminants. While water, e.g. brine, may normally be readily separated from liquid crudes, problems may be encountered with the separation of water from other produced fluids, for example, natural gas condensates which are relatively light, low boiling hydrocarbon fractions produced from natural gas wells. One instance of this problem is in the production of natural gas which has a relatively high water content which leads to undesirable hydrate formation; hydrates normally require removal prior to the shipping of the gas because of their propensity to plug equipment and flowlines. Water removal may usually be effected by the addition of a dehydrating agent or hydrate suppressor such as ethylene glycol followed by separation of the water/glycol phase from the hydrocarbon liquids in the conventional manner. Large quantities of water which are encountered in some gas fields, especially when low ambient temperatures are prevalent, may however make normal processing techniques ineffective or of limited utility. An effective method of water separation would therefore be useful for applications such as this.

[0006] While chemical methods may be used to remove water from the main body of the fuel, they have generally received less commercial acceptance on the large scale used in refinery operations because of the cost factor. Chemical methods, including salt drying, require the replacement or regeneration of the reagents used in the process and the reagents themselves and their products formed by interaction with the water frequently introduce their own complications in subsequent processing. Because the cost of the reagents is directly proportional to the amount of water in the product, physical methods of separation have normally been preferred since their operational cost is not so directly related to the amount of water which needs to be separated.

[0007] Various physical separations have been used including centrifugal separation and filtration, for example, using sand filters. A technique which has, however, become commercially attractive in recent years is liquid/liquid coalescence. See, for example, Refining Details Advances in Liquid/Liquid Coalescing Technology, Gardner’s Refinery, March 1997. The method of coalescing a liquid suspended in another immiscible phase using a coalescing device frequently referred to as a coalescer, has been found useful for removing liquids both from the gaseous phase as in aerosols and from suspensions of one liquid in another liquid with which it is immiscible but may be soluble to a limited degree. Coalescing devices are particularly effective where the volume of liquid to be removed is small in comparison to the volume of the phase from which it is removed so that the technique is of potential application for the separation of small quantities of water from hydrocarbon fuels. The Gardner article discusses the factors that are relevant to the coalescence of droplets of the discontinuous phase from the continuous phase and the ease or difficulty of separation of the immiscible phases. These factors include the physical properties of the phases such as density, viscosity, surface tension and interfacial tension. In addition, the properties of the system such as drop size, curvature of the liquid/liquid interface, temperature, concentration gradients and vibrations may also affect the effectiveness of the coalescence. As noted in U.S. Pat. No. 5,443,724 (Williamson) any or all of these factors may be significant in a particular situation but the density, drop size and interfacial tension of the two liquids appear to be the most significant factors as well as those over the least amount of control can be exercised in affecting the separations.
The type of coalescer employed for the separation depends on the difficulty of separation or coalescence as influenced by the various relevant factors outlined above. The type of fluids being separated frequently determines the nature of the packing used in the coalescence device. Glass fibers have found widespread industrial application in commercial devices. Frequently, however, the presence of surfactants in water/hydrocarbon emulsions lowers the interfacial tension to a value less than about 20 dynes/cm at which the emulsions are stable enough to resist being broken through processing in conventional mesh packing/glass fiber coalescers as well as by other techniques. While electrostatic precipitators may be effective on such emulsions down to interfacial tensions below 10 dynes/cm, their use is rather less favored than the relatively cheaper coalescence method. Surfactants disarm conventional glass filters coalescers by bonding with glass fibers, allowing water molecules to flow through the coalescers with the hydrocarbons. Frequent changes of the cartridge material in the coalescers may obviate this problem but the increased labor and disposal costs associated with frequent cartridge change out are undesirable as is the continued need to monitor the quality of the product to ensure that appropriate specifications are being met. The use of various polymeric materials such as phenolic or acrylic resins which act primarily as binding agents for glass fiber packings may be effective to reduce disarming of coalescers to a significant extent, but the problem remains.

U.S. Pat. No. 5,443,724 discloses a coalescer-separator apparatus which enables longer coalescer cartridge life to be obtained as a result of improved flow distribution within the device. The device is stated to be particularly suitable for the separation of water from organic liquids such as fuels and is capable of achieving extended life using a more compact unit with the same or improved level of performance compared to larger conventional units. As described in U.S. Pat. No. 5,443,724, the coalescence is carried out using a packing material which has a critical wetting surface energy which is an intermediate critical wetting surface tension (CWST) of the discontinuous and continuous phase liquids. This results in the formation of droplets of the discontinuous phase, after which the mixture of the continuous phase liquid and the droplets of the discontinuous liquid are conducted to a separating element which permits the continuous phase to pass (petroleum fuel) to pass substantially resist or prevent passage of the discontinuous phase which can then be separately collected and taken away from the bulk of the product.

Various porous media with differing surface energies are mentioned in U.S. Pat. No. 5,443,724 including polytetrafluoroethylene (PTFE), polybutyleneterephalate (PBT) and other polyfluorinated polymers such as fluorinated ethylene and propylene (FEP) resins. These materials which provide the requisite surface energy to the coalescence/separator filters may be used in the form of a coating of a backing such as glass fiber, stainless steel screens or pleated paper packs. Other media suitable for use as the functional or discontinuous phase barrier material of the separating element are disclosed, for example, in U.S. Pat. No. 4,716,074 (Hurley) and U.S. Pat. No. 4,759,782 (Miller); reference is made to these patents for details of suitable materials for providing the requisite surface properties in coalescence/separator devices.

Normally, separation of liquids by the coalescence technique requires three stages to be successful. First of all, filtration is required to remove fine particles such as iron oxide and iron sulfide that stabilize emulsions and for this purpose, mesh, screen, packed and sand filters are normally satisfactory. Filtration is followed by the coalescence step which, in the case of water and hydrocarbon fuels, is normally accomplished by the use of fluoropolymer membranes which are effective emulsion breakers in liquids with an interfacial tension of greater than about 1 dyne/cm. Separation takes place when the coalesced water droplets are expelled by a hydrophobic barrier membrane, again normally formed from a polymeric material such as fluoropolymer, which permits the hydrocarbon fuel to flow through the cartridge while preventing transfer of the water across the membrane.

Regardless of the details of the coalescence/separator techniques used one problem that remains, particularly in cold climates, is the problem of icing. When the fuel which is to be treated contains relatively high levels of water, low temperatures cause the water to freeze and form ice crystals which plug filters, including the prefilter used in coalescence/separation. Accordingly, regardless of the potential for utilizing the coalescence/separation technique, problems arising from the presence of water in the fuel still remain.

SUMMARY OF THE INVENTION

A method has been devised for the removal of dissolved water or water from hydrocarbon liquid products in a manner which enables the hydrocarbon products to be readily treated by the coalescence/separation technique while reducing the potential for plugging filters and other equipment with ice crystals or solid deposits. According to the present invention, dissolved water or water/ice is removed from liquid hydrocarbons by contacting the feed stream of the hydrocarbon with a liquid treating agent having an affinity for water prior to subjecting the hydrocarbon/treating agent mixture to coalescence/separation to remove the water from the hydrocarbon. The treating agent is separated, together with water removed from the feed stream, from the hydrocarbon product by the coalescence/separation step and recirculated to the feed. The composition of the circulating aqueous phase comprising the treating agent and removed water is controlled to achieve the desired level of water removal to meet relevant product specifications. Consistent with the removal of the water during the coalescence/separation, the water concentration of the circulating treating agent/water blend will tend to increase gradually with transfer of the water in the feed to the circulating fluid. This progressive increase in water content can be compensated by controlled addition of pure treating agent solvent to the recirculating fluid, coincidental with accumulation of the treating agent/water mixture and continuous or periodic dumping of excess mixture. Alternatively, the circulating mixture may be subjected to continuous or batch regeneration or disposed of in any other way which is convenient and economical. The treating agent which finds a wide degree of utility as well as being economically favorable comprises a mixture of (i) water with (ii) a water-hydrocarbon co-solvent. The preferred class of co-solvents are the alcohols, especially methanol, but other water-miscible organic compounds may also be used, as described below. Other, generally less favorable treating agents which may be used include strong aqueous salt solutions, as well as organic and inorganic liquids such as amines or even acids, particularly if it is desired to remove a contaminant from the hydrocarbon which can be reacted with the treating agent or a component of it.
The single FIGURE of the accompanying drawings is a schematic flowchart of a system for removing water from hydrocarbon liquid products using a coalescence/separation technique.

**Detailed Description**

The present invention is applicable to the separation of water, either alone or mixed with other contaminants, from hydrocarbon liquids. The method is particularly applicable to the separation of water from light hydrocarbon liquids of relatively low viscosity, comparable to that of the water to be separated. The method is of particular applicability to the separation of water from refinery hydrocarbon fuels including gasoline (including heavy gasoline and light gasoline), middle distillates such as home heating oil, vaporizing oil, road diesel including all ASTM D2 diesel, kerosene type aviation fuels, as well as potentially to other liquid hydrocarbon product streams which require removal of water in order to meet product specifications or other service or commercial requirements. Normally, the amount of water which is present in these materials prior to separation will be relatively small, typically not more than about 5 volume percent, but product specifications will normally require a much lower water content in order to be acceptable. For example, as noted above, D2 diesel fuel is required to contain no more than 0.2% combined water and sediment and similar requirements will be encountered with aviation kerosenes in view of the very low temperatures encountered by military and commercial jet aircraft at high altitudes. The present separation technique is not dependent upon the chemical composition of the hydrocarbon fuel except to the extent that the chemical composition affects physical properties such as specific gravity, interfacial surface tension, miscibility with water and viscosity. The chemical composition may also affect the degree to which surfactants added during processing or spontaneously formed during the processing (for example, during caustic washing) and the effect the surfactants may have on the other properties, especially emulsion stability, micelle formation, reverse micelle formation.

The present method is also applicable to the separation of water from natural gas liquids also known as natural as condensates. These low viscosity hydrocarbon liquids generally comprise propane, butane and possibly higher hydrocarbons separated from the lower boiling methane and ethane in natural gas from subterranean wells. Natural gas may, as noted above, need to be treated at or near the wellhead to remove either produced water or water combined with various chemicals such as hydrate suppressors, for instance, ethylene glycol, which have been used to treat the produced gas and which have separated out with the liquids as a result of their boiling in the temperature range set for the liquids. Thus, the present invention provides an effective method for the removal of water/glycol (ethylene glycol) mixtures from natural gas liquids.

In the present method, a liquid treating agent which has an affinity for the water in the hydrocarbon feed is mixed with the liquid hydrocarbon before the fuel is subjected to coalescence/separation treatment. The treating agent causes the water and possibly other contaminants to form an aqueous mixture which, when in fully coalesced form, is substantially immiscible with the hydrocarbon although initially it may be suspended in the majority hydrocarbon phase and not readily separable from it by other means. It is this aqueous mixture which is then separated from the hydrocarbon in the coalescence/separation step. During the coalescence/separation treatment, the treating agent and water are separated in the form of a single coalesced phase which is substantially immiscible with the hydrocarbon majority component and recirculated for further addition to the feed. An illustrative schematic of the process configuration is shown in the attached FIGURE by way of example.

The treating agent has for its required effect to have an affinity for the water which is to be removed from the hydrocarbon feed. It may also desirably have an affinity for any other contaminants in the feed which should be removed at this time. For example, if the feed also contains an acidic contaminant such as hydrogen sulfide, the use of an amine as the treating agent may be used to effect removal of the hydrogen sulfide as well as of the water. Conversely, if the feed is, for example, a refinery stream containing basic contaminants such as alkanes from caustic treatment, the use of an acidic treating agent may be effective to remove both water and the residual alkali. The reactive components of the treating agent may make up the entire treating agent or may be added as additive components.

As described in greater detail below, a very useful treating agent is a mixture of water and a co-solvent, miscible with both the alcohol and with the hydrocarbon. This has been found to be very effective in removing water from refinery liquid fuel products such as gasoline and middle distillates such as road diesel, kerojet or heating oil. As noted below, it may also be used with natural gas condensates. One preferred embodiment of the invention is shown in the drawings and is described below by reference to the treatment of a refinery fuel with such a treating agent.

In the FIGURE, a refinery fuel such as mogas, road diesel or kerojet is introduced by way of line 11 to prefilter 12 with the alcohol/water mixture being added through line 13. Prefilter 12 is suitably a mesh or screen filter with additional packing, e.g. compressed glass fibers or polymer (nylon, polyolefin) mesh, adapted to remove fine particulate matter such as iron oxide, silica, which may stabilize emulsions and possibly damage the coalescer/separation units. Use of a high efficiency prefilter such as a sand filter may result in some removal of water.

After passing through prefilter 12, the blend of hydrocarbon, alcohol and water passes through line 14 to coalescence/separation unit 15. Coalescer unit 15 is divided into two stages, comprising a first or coalescence stage 16 and a second or separation stage 17. In the coalescence stage, the suspended particles of water are subjected to coalescence into larger droplets in the presence of a suitable coalescing medium through which the liquids pass in order to effect the desired coalescence of the water, now with the added co-solvent. In separation stage 17, the combined fluids pass over a separation membrane which is selected to have a surface energy favoring passage of the hydrocarbon phase through the walls of the separation membrane while excluding the aqueous phase comprising the co-solvent and the water. The liquid hydrocarbon fuel, now containing only a small and acceptable amount of water passes out of the coalescence/separation unit through line 18 to product storage while the separated co-solvent/water phase, now containing water removed from the original fuel feed, is removed through line 19 for recirculation to the feed. A control valve 20 is provided in the recycle loop under control of manual or automatic control.
controller 21 to permit actuation of the recycle when required. Recirculation is generally not required for operation above freezing point (0° C.) when only the normal coalescence of free water is required, with no hazard of ice crystal formation. When seasonal ambient temperatures drop below freezing, however, and icing and filter plugging are prevalent, injection and recirculation of the co-solvent/water blend can be initiated in order to prevent filter and equipment plugging by ice crystals. Actuation of the injection of the co-solvent/water blend into the feed and recirculation can be initiated either manually or automatically in response to ambient temperature sensors or, preferably, by a pressure sensor on a filter responsive to pressure increase upon plugging with ice crystals.

[0022] The alcohol/water blend passes from control valve 20 to injection line 13 through line 22 with additional co-solvent being injected to the circuit through line 24 in order to maintain the desired co-solvent/water ratio for effective coalescence and separation. As water is progressively removed from the fuel feed, and makeup co-solvent is added, excess co-solvent/water mixture may be purged through the circuit through line 25 and to dump tank 26 from which the blend may be removed through line 27. While it is acceptable to allow an accumulation of water in the recirculation loop up to a permitted maximum set by processing requirements (permissible water concentration in fuel, acceptable co-solvent loss to fuel), it will normally be preferred to maintain the loop at a constant composition ratio between the co-solvent and the water by periodic or continuous addition of co-solvent accompanied by removal of excess circulating liquid. Removal of the excess co-solvent/water may be carried out continuously or periodically or, as an alternative, the gross composition of the recycle loop may be controlled by removal of the water from the co-solvent, for example by distillation, or reverse osmosis to the extent required to maintain constant composition in the recycle loop. Reclamation of the co-solvent in this way is potentially attractive since the regenerated co-solvent is recycled to the process while removing trace contaminants such as salt or trace soaps/surfactants arising from the processing. As an alternative, the co-solvent/water may, depending on the nature of the co-solvent, be disposed of as a relatively clean combustible mixture. With methanol, for example, the methanol/water blend may be used as a low energy content fuel in certain burner and industrial processes, especially if the energy content is maintained above about 18,000 KWh/kg. The exact choice of method by which the composition of the recycle stream is maintained at the desired value is not, however, important and may be selected according to convenience, local economics and other considerations.

[0023] The same technique may be used to separate water/glycol mixtures from natural gas condensates. In this case, similar considerations apply except that the residual water content in the gas may not be as low as required for high quality fuel products, being set, however, by pipelining specifications which may vary according to the temperature conditions prevailing along the pipeline with more stringent specifications prevailing in the colder climates and for undersea pipelines.

[0024] The co-solvent which is used in the blend with the water to promote removal of the water from the hydrocarbon feed is a liquid which is miscible with both water and the hydrocarbon majority component, at least to a limited extent. Organic liquids such as oxygenates are generally suitable and preferred for this purpose in view of their availability, cost and functioning in the present process. While oxygenate esters such as the esters of lower fatty acids and lower alcohols such as ethyl acetate, ethyl propionate, propyl acetate, ethyl butyrate, amyl acetate, esters of the lower alkanols such as methanol, ethanol, propanol and the lower alkoxy-alcohols with lower fatty acids such as hexanoic acid, octanoic acid (e.g. 2-ethyl hexanoic acid), as well as other oxygenates such as the ketones, such as acetone, methyl ethyl ketone (MEK), methyl propyl ketone, aldehydes, ethers such as dimethyl ether and methyl propyl ether, may be used, the preferred co-solvents are alcohols, especially the lower alkanols such as methanol, ethanol and propanol. Alcohols are particularly suited to the removal of water/glycol mixtures from natural gas condensates in view of their miscibility for both the water and the glycol hydrate suppressor.

[0025] The extent to which the co-solvent is required to be miscible with both water and the hydrocarbon is not important as long as the selected co-solvent is miscible with water in all proportions which are used in the process and that the co-solvent has an affinity for water. It is the co-solvent's affinity for water which affects the dehydration of the hydrocarbon e.g. the fuel or NGL (natural gas liquids) and its miscibility with the water which enables the blend of co-solvent and water to be effectively removed from the hydrocarbon by the coalescence technique. The extent to which the co-solvent may be miscible with the hydrocarbon may affect the extent to which the dehydration is completed, a factor which may be significant with fuels. It may also affect the losses of the co-solvent to the hydrocarbons (see below). In order to maintain the loss of co-solvent to the hydrocarbon within acceptable limits a limited miscibility of the co-solvent/water mixture with the hydrocarbon is desirable. For this reason, blends of methanol with water particularly command themselves since blends of these components with high water contents are almost insoluble with hydrocarbon fuels including gasoline as well as NGL.

[0026] The lower alkanols which from the preferred class of co-solvents for use in the present process are those which have a limited solubility in liquid refinery hydrocarbon fuels and NGL. Since the compositions of fuel and NGL may vary, the selected alcohol may vary also. As with other potential co-solvents, the alcohols will be selected for their mutual solubility in hydrocarbons and water as well as their convenient availability and favorable economics. The alcohols may be mono-hydric, dihydric or higher alcohols although mono-hydric and dihydric alcohols (glycols) will normally be preferred. Other functional groups may also be present on the alcohols, for example, ether groups, although halogen will normally not be preferred for reasons of cost, toxicity, and corrosion potential; hydroxymines should normally be excluded in view of their potential to act as surfactants for the hydrocarbon/water system. The preferred monohydric alcohols are methanol and ethanol although propanol may also be used to advantage and glycols such as ethylene glycol, propylene glycol, dipropylene glycol, as well as glycol ethers such as ethylene glycol methylether, diethylene glycol methylether and others will be found suitable. Alcohols with relatively higher solubilities in the hydrocarbon phase may be used at the expense of excessive losses to treated fuels and NGL unless they are combined with relatively high amounts of water, a measure which detracts from the dehydration which is the object of the process. The loss of alcohol or other selected co-solvent to the fuel is not, however, in self rec-
sarily undesirable since the alcohol may act as a deicer in the fuel product, both during distribution and subsequent use, so eliminating the need for a separate deicing additive injection.

[0027] As noted above, however, it is possible and on occasion may be desirable to use alternative treating agents. In order to remove water from hydrocarbon products it is possible, for example, to envisage the use of strong aqueous salt solutions. These have the required affinity for water as a result of their high concentration of mineral salt and, as a result of the removal of the water from the hydrocarbon feed, would become progressively more dilute until their effectiveness ceases. By control of the composition of the circulating fluid stream, e.g. by the addition of more salt and withdrawal of excess volume, it is possible to utilize these salt solutions in the same way as the alcohol/water mixtures referred to above. Sodium chloride solutions will not be found to be optimal in this application but strong solutions of other salts such as calcium chloride or sodium sulfate will be more effective. The use of strong solutions may be found very effective in warmer climates where freezing problems will not be encountered. The use of salt solutions may also be economically favorable. The same simple conventional methods may be used to maintain the concentration of the salt in the solution to restore its functionality as the dehydrating agent, e.g. by the addition of fresh salt and removal of a portion of the circulating volume of liquid or by regenerating the solution, for example, by distillation or membrane separation (osmosis). Alternatively, salt solutions may be cheap enough to be used on a once-through basis with regeneration, particularly if used only intermittently.

[0028] Other materials which have an affinity for water may be used as the treating agent. Liquid amines in particular, commend themselves for this purpose, especially when acidic contaminants such as hydrogen sulfide are to be removed from the hydrocarbon. Amines may be as technically pure compounds or as solutions in water as long as the required affinity for water is retained. Suitable amines for this purpose may include substituted amines such as triethanolamine and diethanolamine as well as simple amines such as monoethanolamine. These treating agents may be useful for removing water simultaneously with acidic contaminants such as hydrogen sulfide or carbonyl sulfide from natural gas liquids.

[0029] The amount of the treating agent, e.g. co-solvent/water blend which is added relative to the feed and the relative amounts of co-solvent and water in the blend are dependent variables to a certain extent. As noted above, a loss of the co-solvent to the hydrocarbon feed does take place but this can be controlled by increasing the amount of water in the blend which is injected into the fuel. On the other hand, the addition of more water detracts from the effectiveness of the dehydration if resort is made to this expedient in order to limit the loss of co-solvent to the fuel. Another factor which requires consideration is the effect of the co-solvent upon the fuel product specifications. Large amounts of the lower alcohols such as methanol and ethanol or other volatile co-solvents, may degrade flash point of treated fuels to an extent that fuel product specifications are not met. Thus, increasing the relative amount of water in the mixture may be effective for controlling changes in flash point during the treatment process although possibly at the expense of diminished effectiveness for water removal. The higher alcohols such as dipropylene glycol, however, may be added to distillates after the water removal process to act as high flash point deicers during subsequent distribution and use. In general, however, the loss of co-solvent to natural gas liquids will represent merely an economic loss of the process rather than having a major effect on the product (NGL) quality.

[0030] The amount of water in the co-solvent/water blend will depend upon the selected co-solvent, its solubility in the hydrocarbon components of the fuel or other hydrocarbon liquid, the ratio of water/co-solvent blend to the hydrocarbon, operating temperature and other factors. Taking the lower alcohol, methanol, as the selected solvent, the ratio of methanol to water will normally vary between 20/80 and 80/20 by volume. This ratio will vary with other alcohols and other co-solvents according to the specific alcohol or other co-solvent selected, its solubility characteristics with water and the hydrocarbon and the extent to which transfer of the alcohol to the hydrocarbon fuel can be tolerated and the amount of water in the initial hydrocarbon feed. Normally, however, with methanol as the alcohol, the volume ratio of alcohol and water will be from about 75:25 to 25:75 with approximately 50:50 blends being normally adequate.

[0031] The preferred alcohol for use in the present process is methanol which is selected not only for its low cost, low viscosity and boiling point (if reclaiming is desired) but also for its effectiveness in dissolving solid ice when present. A 50:50 methanol/water blend has been found to be extremely effective and this ratio is sufficiently concentrated to dehydrate the fuel down to low water levels. The freezing point of a 50:50 methanol/water mixture is below 40° C. so the process is capable of operating over wide temperature limits from less than -40° C up to relatively high ambient temperatures. This represents a very useful working range, especially for use with fuel treatment in cold climates and for gas condensate treatment when low temperature gas pipeline specifications have to be met. Methanol has the additional advantage that loss to the hydrocarbon fuel majority component is relatively small, as compared to higher alcohols and for this reason, process losses may be minimized. Combinations of alcohols such as methanol with dipropylene glycol may be used when it is desired to achieve some losses to fuels in order to provide residual deicing capability for the treated fuel product.

[0032] The amount of the co-solvent/water blend which is added to the hydrocarbon feed is typically less than 10% by volume of the total feed although the exact amount selected will be depend upon the degree of dehydration desired, the co-solvent e.g. alcohol selected, the ratio of water to co-solvent in the blend and any relevant product specifications such as flash point for treated fuel products. Also relevant would be the ratio of water and glycol in treating natural gas condensates which have been treated with glycol hydrate suppressor. Normally, in the case of alcohol/water blends, the amount of the alcohol/water blend will be from 0.1% to 10% by volume of the total fuel feed and in most cases from 0.5% to 5% of the feed will be found sufficient. In many cases, about 1% by volume of the feed will be adequate with the 50:50 methanol/water blend selected for the dehydration.

[0033] The prefiltration which are used ahead of the coalescer may be any suitable type of conventional filter, including sand filters, metal or polymer meshes, or other porous material capable of removing small solid particles which would tend to stabilize the fuel/water emulsions and which might result in damage to the more delicate coalescer membranes. Polyester and nylon mesh filters are suitable, typically with crush strengths in the range of 70-145 kg.cm⁻² (75-150 psi) and
other non-woven filter materials may be used as convenient alternatives. The filter material may be contained in a conventional filter housing and the filter material in any convenient configuration which provides the desired filter life, filtration capacity and flow rate, for example, pleated mats, cylindrical sheets or mats, helical or spirally wound mats.

[0034] In a similar manner, the material of the coalescer and separation elements in the coalescing unit and the separation unit may be provided in a form which provides the necessary mechanical strength, liquid flow rate and unit life. In the simplest form, the media serving as the coalescer and separator materials may be provided in sheet form which may be formed either as flat sheets, pleated or corrugated sheets or in other suitable arrangements e.g. cylindrically, helically or spirally wound sheets, as disclosed in U.S. Pat. No. 5,443,724 to which reference is made for a disclosure of suitable coalescer and separator materials and configurations for them.

[0035] The coalescer promotes the coalescence of the discontinuous or highly divided phase of the hydrocarbon/water mixture in which the water is in the form of finely divided droplets which are immiscible with the hydrocarbon phase into larger and coarser droplets. The coalescer and separator media is used in the form of a packing in which the material has a critical wetting surface energy intermediate the surface tensions of the liquids forming the continuous and discontinuous phases, that is, of the hydrocarbon majority component and the water which is to be removed. In practice, this means that the medium needs a surface energy of less than about 72 dynes/cm. Similarly, the material of the separating element is selected so as to have a surface energy which permits passage of the majority hydrocarbon component through the small pores of the separator media but to preclude transfer of the water across the wall. In this case, since water is the discontinuous phase which is to be separated (along with the alcohol/water injected) the separator media are selected to have a critical surface energy (CWST) below the surface tension of water which is typically about 72 mN m⁻¹. As disclosed in U.S. Pat. No. 5,443,724, materials preferred for use as the phase barrier material for the separator include silicates, such as silicone treated paper and more preferably fluoropolymeric materials of which fluorocarbons or perfluorocarbons (perfluor resins) are particularly preferred. Examples of preferred materials for use as the packing or coating in the separator include polytetrafluoroethylene (PTFE) or other polytetrafluoroethylene polymers, such as fluorinated ethylene propylene (FEP) or other fluoropolymer resins. As noted, a preferred separator material includes a coating of one of these materials on a stainless steel screen or a pleated paper pack. Other suitable materials include those disclosed in U.S. Pat. No. 4,759,782 to which reference is made for a disclosure of such materials. Generally, the phase barrier material which acts to prevent the discontinuous phase passing through it (and is therefore appropriately referred to as the discontinuous phase barrier material) is selected to have pores smaller than a substantial amount of the droplets of the liquid which forms the discontinuous phase. Typically, the pore size of the functional part of the separator material is selected to be from 5 to 140 microns, preferably 40 to 100 microns. When, as in this case, the discontinuous phase is water, the pore size is preferably approximately 80 microns.

[0036] The coalescing unit and the separation unit may suitably be contained in a housing which provides and adequate number of coalescing/separating elements with these elements being suitably arranged inside the housing for reasons of functionality and operating convenience. A suitable arrangement is shown in U.S. Pat. No. 5,443,724, using coalescer and separator cartridge elements arranged in superposed relationship with one another in a cylindrical type housing which permits ready access to the cartridges when they require replacement. However, other configurations may be used and reference is made to commercial suppliers of this equipment including Pall Corporation of East Hills, N.Y. 11548.

We claim:
1. A method for removing water or water and ice from a liquid hydrocarbon, which comprises:
   contacting the feed stream of the hydrocarbon with a treating agent having an affinity for water which is immiscible with the hydrocarbon,
   subjecting the mixture of hydrocarbon and treating agent to coalescence/separation to coalesce the non-hydrocarbon components of the hydrocarbon/water/treating agent mixture to form larger size coalesced liquid droplets,
   separating the coalesced liquid droplets comprising water and treating agent from the hydrocarbon to form a dehydrated hydrocarbon product,
   recirculating water and treating agent separated from the hydrocarbon as a recycle blend to the feed stream of the hydrocarbon.
2. A method according to claim 1 in which the treating agent comprises a mixture of water and a co-solvent for water and the fuel
3. A method according to claim 2 in which the co-solvent comprises an alcohol.
4. A method according to claim 3 in which the alcohol comprises a lower monohydric alcohol or a lower dihydric alcohol.
5. A method according to claim 3 in which the alcohol comprises methanol, ethanol, propanol, ethyleneglycol, propyleneglycol or dipropyleneglycol.
6. A method according to claim 4 in which the alcohol comprises methanol.
7. A method according to claim 1 in which the mixture of hydrocarbon feed and the blend of treating agent and water is separated by a three stage separation sequence comprising filtration, coalescence of water and separating agent into droplets and separation of the coalesced liquid droplets.
8. A method according to claim 2 in which the volume ratio of the co-solvent/water blend to the hydrocarbon feed is from 0.1 to 10 volume percent.
9. A method to claim 2 in which the volume ratio of the co-solvent to the water in the blend which is mixed with the hydrocarbon feed is from 80:20 to 20:80 co-solvent:water.
10. A method according to claim 9 in which the volume ratio of the co-solvent to the water in the blend which is mixed with the hydrocarbon is from 60:40 to 40:60 co-solvent component: water.
11. A method according to claim 1 in which the water concentration of the recirculating treating agent/water blend gradually increases with removal of the water from the feed.
12. A method according to claim 1 in which the composition of the recycle blend is controlled to achieve the requisite level of water removal for the hydrocarbon product to meet relevant product specifications.
13. A method according to claim 12 in which the composition of the recycle blend is controlled by addition of treating agent to the recycle blend.
14. A method according to claim 13 in which a portion of the recycle blend is removed from the recirculation.

15. A method according to claim 1 in which the mixing of the treating agent and water blend with the hydrocarbon feed is initiated by automatic control responsive to an indication of ice crystal accumulation in the hydrocarbon.

16. A method according to claim 1 in which the hydrocarbon comprises a petrolean refinery liquid fuel product.

17. A method according to claim 16 in which the fuel product comprises a gasoline or middle distillate fuel product.

18. A method according to claim 17 in which the middle distillate fuel product comprises a road diesel fuel.

19. A method according to claim 1 in which the hydrocarbon comprises natural gas liquids.

20. A method according to claim 19 in which the natural gas liquid feed comprises natural gas liquids, water and glycol and in which the glycol is separated from the natural gas liquids with the water.

* * * * *