(51) International Patent Classification:
C10G 50/00 (2006.01)

(21) International Application Number:
PCT/ZA2006/000029

(22) International Filing Date:
24 February 2006 (24.02.2006)

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:
60/657,140 28 February 2005 (28.02.2005) US

(71) Applicant (for all designated States except US): THE PETROLEUM OIL AND GAS CORPORATION OF SOUTH AFRICA (PTY) LTD [ZA/ZA]; 151 Trans Conrado, Parow, 7500 Cape Town (ZA).

(72) Inventor; and

(75) Inventor/Applicant (for US only): MINNIE, Rudolph, Ockert [ZA/ZA]; No. 40 21st Avenue, 6500 Mossel Bay (ZA).

(74) Agent: HAHN & HAHN INC, WHEELER, CJ; DUNLOP, AJ; WILLIAMS, WV; LUTEREK, JF; MICHAEL, C; VENTER, PRC; BERND; 222 Richard Street, Hatfield, 0083 Pretoria (ZA).

(54) Title: CATALYTIC CONVERSION OF OLEFIN TO DIESEL AND GASOLINE FUEL

(57) Abstract: The invention provides a method of controlling a COD reactor. The method includes analysing the reaction mixture from the COD reactor to determine a selected alkene to alkane ratio, which is representative of the conversion rate of the reactor.
Title: Catalytic Conversion of Olefins to Diesel and Gasoline Fuel

Technical field of the invention

This invention relates to catalytic conversion of olefins to diesel and gasoline fuel (COD). More particularly, it relates to a method of controlling a COD reactor.

Background to the invention

A COD reactor oligomerises lower olefins such as Propylene, Butylene and C₅ to 120°C light olefins to heavier olefins, which are in the boiling range of gasoline and diesel. Normally the catalyst is a zeolite such as an aluminium silicate catalyst. The feed stream is catalytically converted to a product stream which is distilled to produce propane, butane, C₅⁺, gasoline (C₁₂ Range) and distillate. The reactor can be selectively operated to produce predominantly gasoline or distillates. A COD reactor normally operates in a discontinuous manner due to residual heavy hydrocarbon deposits formed on the catalyst during normal operation and the loss of catalyst reactivity. At the end of the catalyst cycle, the operation is discontinued and catalyst regenerated. In order to have a continuous product stream, three or more reactors are operated in a staggered sequence.

Reactor control is important to respectively produce predominantly gasoline or distillates within required product specifications. The product slate is influenced by parameters such as weighted average reactor bed temperatures (WABT), reactor space velocity, feed composition variation, recycle rate and composition, reactor pressure, and the catalyst reactivity. A higher WABT will result in more distillates in the product slate. A heavier hydrocarbon recycle stream to the reactor will also result in more distillates in the product slate. The product slate is further influenced by the catalyst
reactivity, which is determined by the progress of the catalyst cycle. To compensate for loss of catalyst reactivity, the WABT is increased as the catalyst cycle progresses.

It will be appreciated that due to the various influencing factors and its interplay it is important to monitor the conversion in the reactor to ensure a desired product slate. The applicant is aware that this is done by measuring the distilled product viscosity. Distillates, for example, normally have a viscosity of about 2.4 centistokes measured at 40°C. For an average 126 m³ inventory (i.e. 42m³x3) size reactor, the distilled product is available downstream from the reactor after and average of 8 hours, or after a volume of 450m³ distillate of product has been produced. This method of monitoring the conversion in the reactor stream only allows a delayed adjustment of reactor operating conditions if the viscosity suggests that the product slate is not as required. This could cause over or under conversion, unwanted aromatics formation, unwanted n-paraffin to iso-paraffin ratio or undesired octane or cetane number, as the case may be, in the product slate produced in the delay time or volume. It will also be appreciated that the monitoring of the effect of any adjustments of the reactor parameters will also be delayed.

General description of the invention

According to a first aspect of the invention there is provided a method of COD reactor control, which method includes:

analysing the reaction mixture from the COD reactor to determine a selected alkene to alkane ratio, which is representative of the conversion rate of the reactor.

The method may include the step of extracting a representative sample of the contents of the reaction mixture from the COD reactor.
The analysing step may include determining the butylene to butane ratio or, preferably, the propylene to propane ratio.

Table 1 gives the relationship between Propylene content in the propane rundown/off gas streams and the overall propylene conversion rate across the entire reactor system.

Table 1 also gives the relationship between Butylene content in the propane rundown/off gas streams and the overall byutylene conversion rate across the entire reactor system.

<table>
<thead>
<tr>
<th>Propylene content in Off gas (mol%)</th>
<th>0.0</th>
<th>0.1</th>
<th>0.3</th>
<th>1.1</th>
<th>1.3</th>
<th>4.0</th>
<th>5.0</th>
<th>6.4</th>
<th>7.7</th>
<th>8.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene conversion (mol %)</td>
<td>100.0</td>
<td>99.9</td>
<td>99.9</td>
<td>99.8</td>
<td>99.8</td>
<td>98.0</td>
<td>97.0</td>
<td>97.0</td>
<td>96.7</td>
<td>95.5</td>
</tr>
</tbody>
</table>

| Butylene content in Off gas (mol%) | 0.2 | 0.7 | 4.0 | 8.0 | 7.4 | 4.0 | 4.0 | 5.4 | 5.4 | 6.7 |
| Butylene conversion (mol %)        | 99.5 | 96.4 | 94.4 | 95.0 | 94.0 | 88.0 | 86.2 | 84.8 | 85.9 | 78.8 |
The method may include the step of determining the optimum ratio of the selected alkene to alkane for a specific feed stream and product slate.

The method may include the step of determining which reactor parameters to adjust to obtain the optimum ratio of alkene to alkane for a specific feed stream and product slate.

The method may include the step of determining reactor parameters related to the alkene to alkane ratio and adjusting the parameters to obtain the optimum ratio of alkene to alkane for a specific feed stream and product slate.

Table 2.3 displays the temperature gradient that is used to adjust the temperature profile across each reactor. As soon as the propylene and butylene content increase in the propane rundown stream, reactor temperatures are increased with increments of 0.5°C per day at the inlet of the each reactor.

The method may include the step of adjusting the reactor parameters.

**Detailed description of the invention**

The invention is now described by way of example with reference to the accompanying flow diagram of a typical COD plant.

Referring now to the flow diagram, Figure 1, of a COD plant, in accordance with the invention.

COD is the abbreviation for Catalytic Conversion of Olefins to Diesel and Gasoline fuel. The COD process converts propylene, butylene and C5 – 120°C light olefins to heavier olefins, which are in the boiling range of gasoline
and diesel, by means of oligomerisation over a zeolite (Aluminium Silicate) catalyst.

The COD plant produces propane, butane, C₅⁺ gasoline and distillate. The olefinic hydrocarbon product covers a wide range of carbon numbers, which starts with a very small amount of Propylene (C₃⁺) and ends with a heavy hydrocarbon distillate (C₂₃⁺). The distribution curve shows a dominant peak in the gasoline range (C₁₂⁺).

The COD plant is designed to operate under two extreme operating modes. When the unit is operated at design feed rate under the high distillate mode the unit will produce 66% mass distillate.

The design capacity on a high distillate mode is therefore:

\[
\frac{44827 \text{ kg/h distillate yield}}{67489 \text{ kg/h total fresh feed}} = 66 \% (\text{m/m}) \text{ distillate product}
\]

The design conversion rate for the distillate mode per pass falls from 99 % for C₃⁺ to 19 % for C₈⁺.

The hydraulic design of the unit also considers an alternative case where the overall distillate yield is assumed to be as low as 40% mass on total feed. This case is referred to as the high gasoline mode.

The design capacity on a high gasoline mode is:

\[
\frac{26725 \text{ kg/h distillate yield}}{67489 \text{ kg/h total fresh feed}} = 40 \% (\text{m/m}) \text{ distillate product}
\]
The main difference between the gasoline and distillate mode are higher weighted average reactor bed temperature (WABT) and heavier molecular weight gasoline recycle stream for the distillate mode. Distillate is defined as the product that meets a viscosity specification of 2.4 centistokes (cSt) measured at 40°C.

Thus, when the unit is operated at design feed rates/ratio's of propylene, butylene and C₅ - 120°C light olefinic hydrocarbons, under high distillate mode, it will produce 66 % mass distillate per total mass of fresh feed.

The COD plant requires a discontinuous operation, due to the residual heavy hydrocarbon deposits formed on the catalyst during normal operation. The catalyst needs to be regenerated in-situ under a nitrogen circulation with small quantities of oxygen from time to time in order to remove the carbon.

The term "catalyst cycle" shall mean that period commencing with the first contact of feed stock with fresh or newly regenerated COD catalyst, and terminated when the outlet temperature of any of the three reactors of a specific train has reached the maximum catalyst temperature of 350°C.

Depicted in Table 2.3 is the typical Rx inlet temperature and outlet temperature profile from the start of a run to the end of a run condition, displayed over a 15-day catalyst cycle.

The catalyst cycle length will be determined by the mode of operation. Distillate mode will be a more severe operation than that of Gasoline mode, which means that the catalyst will have to be regenerated more frequently if the unit is operated in the Distillate mode.
The reactor section consists of the feed system and the three parallel reactor trains. The feed and the recycle streams are pressurised and heated in the feed system, and sent separately to the reactor trains. Both streams are mixed and enter into one or two trains in parallel, at reaction conditions. While these trains are receiving/processing feed, the third train is being regenerated or is on standby.

The conversion of light olefins to a mixture of higher molecular weight olefins takes place over the COD catalyst in the reactors. Each train consists of three reactors arranged in series. In order to limit the temperature increase across the catalyst bed a portion of the reactor product is returned to the reactor feed as recycle. This serves two main functions:

1. The large quantity of recycle acts as a heat sink for the heat generated by the exothermic oligomerisation/polymerisation reaction.
2. Un-reacted olefins are given a second chance to react, thus increasing the overall conversion.

The catalyst deactivation occurring during normal conversion services is compensated for, by raising the reaction temperature on all three reactors very slowly.

Catalyst regeneration is required as soon as the maximum allowable catalyst temperature has been reached. At this stage, called end of cycle, swinging from that train to the freshly regenerated train allows for the continuation of the operation.

The most important reaction over the zeolite catalyst is olefin oligomerisation.
The oligomerisation reactions means the conversion of light olefins, mainly C$_3^-$ to C$_8^-$ to mixtures of higher molecular weight olefins over the COD catalyst.

\[ C_A^- + C_B^- \leftrightarrow C_{A+B}^- \]

A = 3 .......8 mainly
B = 3 .......8 mainly

The olefin product covers a wide range of carbon numbers, which starts with a very small amount of propylene (C$_3^-$) and ends with a heavy hydrocarbon distillate (C$_{23}^-$). The distribution curve shows a dominant peak in the gasoline range (C$_{12}^-$).

For the selected COD catalyst the conversion per pass for C$_3^-$ to C$_8^-$ depends on the feed composition, reactor pressure, reactor temperature and the liquid hourly space velocity (LHSV). However the most important variable for adjusting the conversion i.e. product quality is the reaction temperature.

The overall reaction is exothermic and very sensitive to temperature. This sensitivity is reduced by the use of recycled gasoline stream, i.e. less active paraffinic material. In addition the gasoline recycle improves the distillate yield. The reaction temperature is increased to compensate for the catalyst deactivation and hence to maintain the design conversions. The temperature, however, cannot be increased indefinitely and the maximum allowable reaction temperature defines the end of catalyst cycle.

Compared to the gasoline mode the distillate mode operation requires higher conversions. This is achieved through higher weighted average reactor inlet temperatures (approximately 10°C higher WAIT)
The design conversion per pass falls from 99 % for C₃ for the distillate mode, while the conversion rate falls from 92 % for C₃ for the gasoline mode.

Apart from the olefin conversions, other components in the reactor feed streams are converted as follows:

- Alcohols are hydrogenated to olefins.
- Ketones (MEK – Methyl Ethyl Ketones) are partly hydrogenated to water and olefins.
- Aromatics partly react with olefins to form poly-alkylated aromatics.

**Process Variables**

The COD plant is a combination of a chemical process and physical separation. The following process variables influence the product quality:

- Reactor space velocity (determined by the fresh feed rate).
- Feed composition variation.
- Recycle rate and composition.
- Reactor pressure.
- Reactor temperature.

**Reactor space velocity**

The space velocity is normally defined by the ratio of the feed in mass units to the mass of the catalyst in the reactor at specific conditions. Assuming a constant recycle feed to the reactors, the weighted hourly space velocity (WHSV) expresses the amount of fresh feed in kg per hour with reference to one kg of catalyst. The design figure is 0.5 kg/(h.kg). Total fresh feed to one train is 33745 kg/h and the total mass of catalyst loaded into one train is 67489 kg.
Fresh feed load  =  Combined fresh feed (kg/h)
                  Total catalyst loaded (kg)

Therefore the   WHSV   =  \[ \frac{33745 \text{ kg}}{67489 \text{ h kg}} \]
                  \[ = 0.5 \text{ h}^{-1} \]

Raising the WHSV requires an increase in reaction temperature to
achieve a fixed conversion. This will shorten the operation cycle and reduce
the catalyst lifetime.

**Reactor temperature**

Catalyst temperature is the most important variable in controlling the
oligomerisation reaction. The temperature at the start of the cycle should be
the lowest value that results in an acceptable distillate quality.

The term catalyst cycle means the period commencing with the first
contact of feed stock with fresh or newly regenerated COD catalyst, and
terminating when the outlet temperature of any one of the three reactors of a
specific train has reached the maximum catalyst temperature of 350°C.
Catalyst cycle lengths were estimated to be in the order of ±30 days.

The maximum temperature for catalyst is 350°C, which is also defined as
the end of catalyst cycle (EOC) conditions. An important guideline is that the
reaction temperature must be kept as low as possible for as long as possible
in order to maximise catalyst cycle time and catalyst lifetime.

The reactor (WAIT) inlet temperature at the start of run conditions for
the distillate mode is 233.3 °C.
Rx 1 inlet = 220°C, Rx 2 inlet = 230°C & Rx 3 inlet = 250°C

\[
\text{WAIT} = [(220 \times 0.333^\circ \text{C}) + (230 \times 0.333^\circ \text{C}) + (250 \times 0.333^\circ \text{C})] = 233.3^\circ \text{C}
\]

The catalyst loaded into a reactor train is divided into three equal quantities. Therefore a weighing factor of 0.333 is used for each reactor.

Furthermore, in order to control the exothermic reaction within a reactor and to prevent equipment and catalyst damage, a limit on the differential temperature of 30, 31 and 7°C was imposed on the first, second and third reactor respectively under distillate mode operation.

Inlet temperature minus outlet temperature at start of catalyst cycle, e.g.

- Reactor 1 = 220 - 250 = 30°C
- Reactor 2 = 230 - 261 = 31°C
- Reactor 3 = 250 - 257 = 7°C

Total differential temperature across all 3 reactors in distillate mode is therefore limited to 68°C. The reactor (WAIT) inlet temperature at the start of run conditions for the gasoline mode is 223,1 °C.

Rx 1 inlet = 210°C, Rx 2 inlet = 220°C & Rx 3 inlet = 240°C.

\[
\text{WAIT} = [(210 \times 0.333^\circ \text{C}) + (220 \times 0.333^\circ \text{C}) + (240 \times 0.333^\circ \text{C})] = 223.1^\circ \text{C}.
\]

Displayed in Table 2.3 is the typical temperature profile for the three reactors when operated in distillate mode.
In order to control the exothermic reaction within a reactor and to prevent equipment and catalyst damage, a limit on the differential temperature of 20, 20 and 20°C was imposed on the first, second and third reactor respectively under gasoline mode operation.

Inlet temperature minus outlet temperature at start of catalyst cycle, e.g.

- Reactor 1  =  210 – 230 = 20°C.
- Reactor 2  =  220 – 240 = 20°C.
- Reactor 3  =  240 – 260 = 20°C.

Total differential temperature across all 3 reactors in gasoline mode is therefore restricted to 60°C.
Table 2.3 - Reactor temperature profile for reactor inlet and outlet temperatures of the commercial COD plant

**Reactor 1**
- Start of Catalyst cycle
- Rx 1 delta T = 30°C
- End of Catalyst cycle

**Reactor 2**
- Start of Catalyst cycle
- Rx 1 delta T = 31°C
- End of Catalyst cycle

**Reactor 3**
- Start of Catalyst cycle
- Rx 1 delta T = 7°C
- End of Catalyst cycle
The feed and product streams

Displayed in Table 3 below are the design figures of the feed and product streams for the COD commercial unit at PetroSA.

<table>
<thead>
<tr>
<th>Table 3 - COD feed and product streams</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FEED</strong></td>
</tr>
<tr>
<td>Propylene</td>
</tr>
<tr>
<td>Butylene</td>
</tr>
<tr>
<td>C5/C6 olefins</td>
</tr>
<tr>
<td>Hydrogen</td>
</tr>
<tr>
<td><strong>PRODUCTS</strong></td>
</tr>
<tr>
<td>Distillate</td>
</tr>
<tr>
<td>Gasoline</td>
</tr>
<tr>
<td>Butane</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Fuel gas</td>
</tr>
<tr>
<td>Waste water</td>
</tr>
</tbody>
</table>

Reactor pressure

For the oligomerisation process, it is known that a higher pressure improves the conversion and that the reaction product moves towards higher carbon numbers. However, the maximum operating pressure is limited by economics. For this reason the operating pressure of the reactors is fixed at 5800 kPa(g) for conversion service.

Previously the viscosity of the tail end of the unit was used as a controlling medium, in particular to see if the distillate run down is on spec. The control parameter of 2.4 cst @400°C ±0.1cst was used. Any deviation of typical value (2.4 cst) requires reaction temperature adjustment in all reactors.
This control parameter was tedious with a lag period of at least 8 hours which results in "off-spec" distillates of ~450 m³. The unit consists of 9 reactors, three reactors per train. Normally 2 trains are in conversion mode and 1 train is in catalyst regeneration mode. One reactor has an inside diameter of 3.1 meter and tangent to tangent (T/T) of 5 meters. Reactor volume is ±45 m³. Such viscosity analysers and the results are also not always reliable.

In order to improve product loss due to off-spec distillate an easier and more controllable method was developed. Extensive tests by the applicant have proved that by measuring the propylene/butylene conversion rates across the unit is far more superior and reliable than the viscosity methods. Instantaneous adjustment to reactor temperature and fresh feed (FF) and recycle feed (RF) ratios can be made to counteract deviations in the final distillate product.

Control conversion
Propylene : 97 – 99 mol%
Butylene : 88 – 95 mol%

Too high propylene and butylene conversion rates result in low gasoline octane number. High conversion also results in product cracking.
Too low propylene and butylene conversion rates result in reduced distillate production and/or off-spec distillate.

If propylene and butylene conversion rates decreases, the following parameters can be adjusted.

- Increase all six reactor inlet temperature, see temperature range Table 3.2
- Reduce the fresh feed (FF) to recycle Feed (RF) ratio, typically RF:FF = 2.5:1 mass/mass for old catalyst and 30:1 for fresh or newly regenerated catalyst.
If conversion rates decrease towards the end of catalyst cycle, RF:FF ratio is reduced to not less than 2:1.
Claims

1. A method of controlling a COD reactor, which method includes the step of:
   analysing the reaction mixture from the COD reactor to determine a selected alkene to alkane ratio, which is representative of the conversion rate of the reactor.

2. A method as claimed in Claim 1, which includes the step of extracting a representative sample of the contents of the reaction mixture from the COD reactor.

3. A method as claimed in Claim 1 or Claim 2, wherein the analysing step includes determining the butylene to butane ratio or the propylene to propane ratio.

4. A method as claimed in any one of the previous claims which includes the step of determining the optimum ratio of the selected alkene to alkane for a specific feed stream and product slate.

5. A method as claimed in Claim 4, which includes the step of determining reactor parameters related to the alkene to alkane ratio and adjusting the paramaters to obtain the optimum ratio of alkene to alkane for a specific feed stream and product slate.

6. A method of controlling a COD reactor substantially as herein described and illustrated.
Figure 1
### INTERNATIONAL SEARCH REPORT

#### A. CLASSIFICATION OF SUBJECT MATTER
**INV. C10G 50/00**

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

**C10G**

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO–Internal, WPI Data, PAJ

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 5 034 565 A (HARANDI ET AL) 23 July 1991 (1991-07-23) column 3, line 58 – column 4, line 3 column 5, line 18 – line 32 column 7, line 5 – line 21 column 8, line 24 – line 54; claims 1,9</td>
<td>1–6</td>
</tr>
<tr>
<td>X</td>
<td>US 4 899 014 A (AVIDAN ET AL) 6 February 1990 (1990-02-06) column 4, line 47 – column 5, line 48; claim 1; example 4</td>
<td>1–6</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 375 286 A (MOBIL OIL CORPORATION) 27 June 1990 (1990-06-27) page 7, line 42 – page 9, line 46; claim 1</td>
<td>1–6</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

* **A** document defining the general state of the art which is not considered to be of particular relevance
* **E** earlier document but published on or after the international filing date
* **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* **O** document referring to an oral disclosure, use, exhibition or other means
* **R** document published prior to the international filing date but later than the priority date claimed

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

**Y** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

**S** document member of the same patent family

**Date of the actual completion of the international search**

27 June 2006

**Date of mailing of the international search report**

04/07/2006

**Name and mailing address of the ISA/**

European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk

Tel. (+31-70) 340-2040, Tx. 31 851 epo nl, Fac. (+31-70) 340-3016

**Authorized officer**

Deurinck, P
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 5034565</td>
<td>23-07-1991</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>US 4899014</td>
<td>06-02-1990</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 4693289 A</td>
<td>21-06-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2005452 A1</td>
<td>19-06-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 68915258 D1</td>
<td>16-06-1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 68915258 T2</td>
<td>01-09-1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 2222489 A</td>
<td>05-09-1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 4939314 A</td>
<td>03-07-1990</td>
</tr>
</tbody>
</table>