

## Chapter 7

### Results on isomerization of 1-Octene

The results of the products obtained from the reaction of 1-Octene with the three catalysts will be dealt with differently than for 1-butene and 1-hexene since it was more difficult to identify compounds present in the liquid product. This Chapter will deal with the following aspects:

- Spiking with known compounds;
- Kováts indices and retention time calculations;
- Selectivity;
- Conversion;
- Coking; and lastly
- Comparison of the three catalysts.

The first two sections will deal with identifying components in the liquid product samples.

#### 7.1 Spiking with known compounds

The liquid reaction product of 1-octene over the Siralox 40 catalyst at 350 °C was analyzed by GC and further used for the purposes of component identification. (Figure 7.1). Spiking of the product with 1-octene was used to verify the products formed.

##### *1-octene added to unspiked reaction product sample*

A drop of 1-octene was pipetted into a vial and diluted with some of the liquid product mentioned in the previous paragraph. The GC spectra of the unspiked liquid product sample (Figure 7.1) and the spiked sample were overlayed and the 1-octene peak was identified by the increase in peak height (Figure 7.2).

##### *Trans-2-octene added to unspiked reaction product sample*

A drop of *trans*-2-octene was pipetted into a vial and diluted with some of the liquid product as stated before. The GC spectra of the unspiked liquid product sample (Figure 7.1) and the spiked sample were overlayed and the *trans*-2-octene peak was identified by the increase in peak height (Figure 7.3).

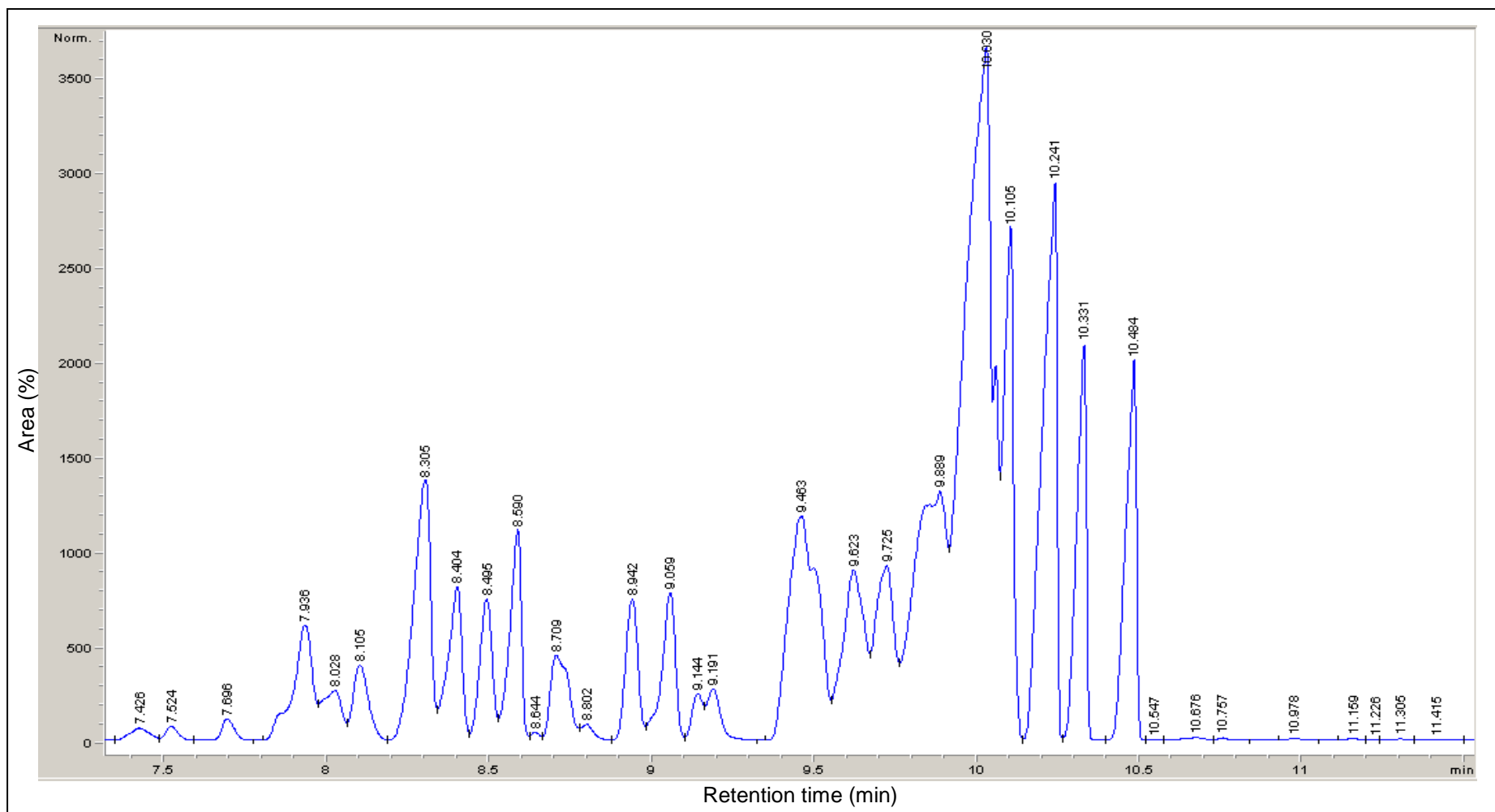


Figure 7.1: Unspiked liquid reaction product of 1-octene over Siralox 40 catalyst at 350 °C

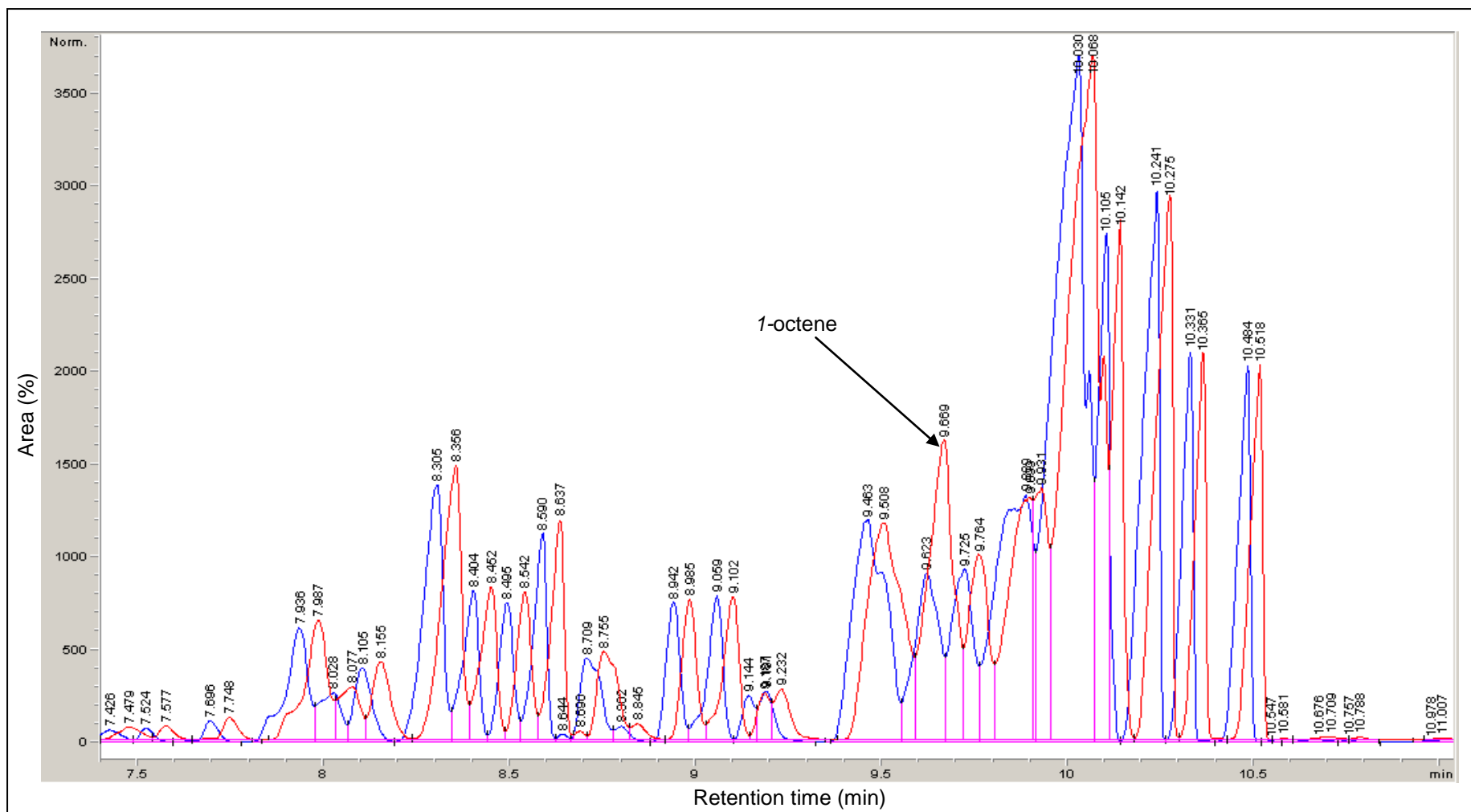


Figure 7.2: 1-Octene added to unspiked reaction product sample

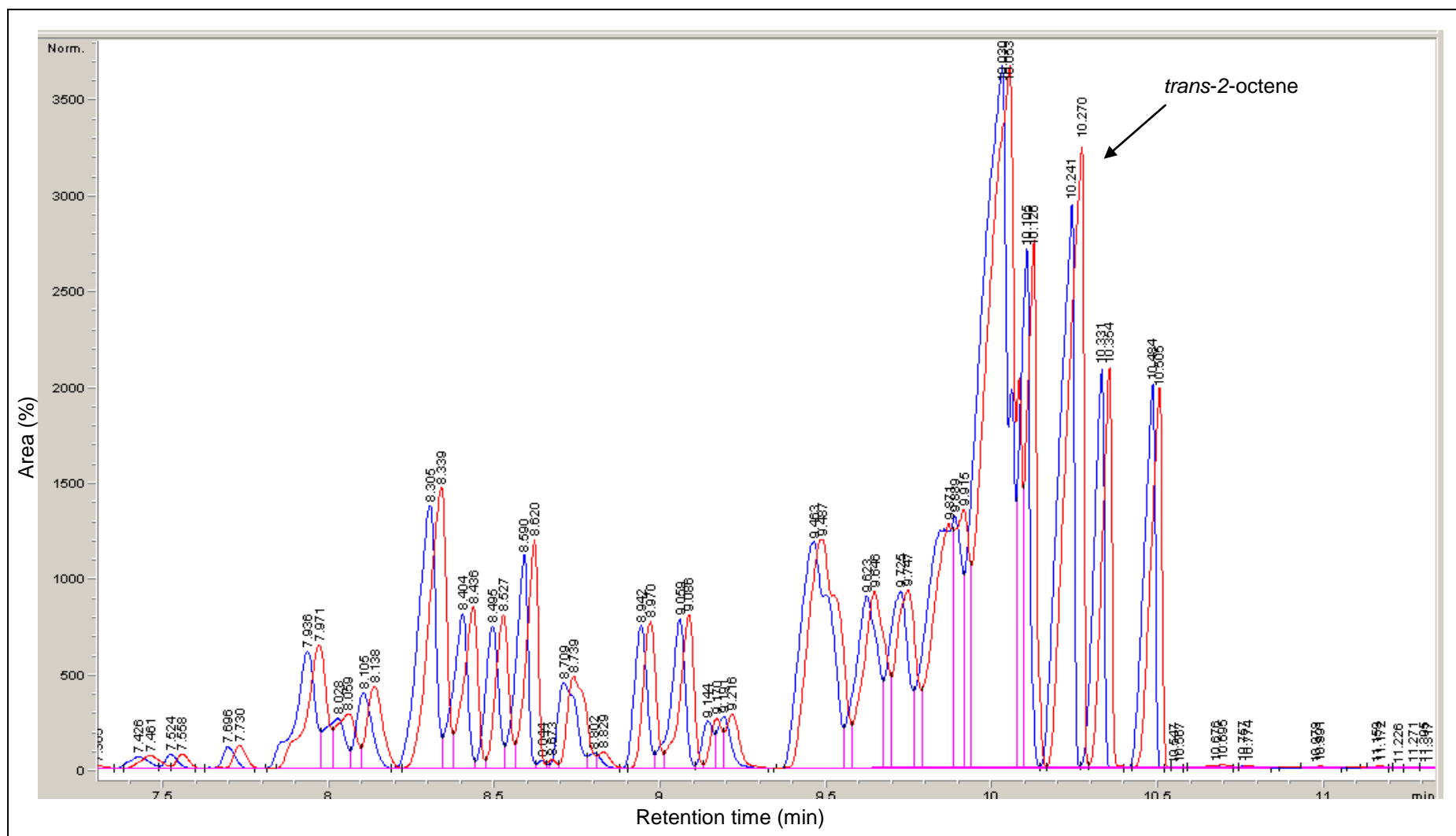


Figure 7.3: *Trans*-2-octene added to unspiked reaction product sample

A shift in retention times was observed with the overlays in Figure 7.2 and 7.3 but it was not that significant to make a difference on the results.

*Trans-3-octene added to unspiked reaction product sample*

A drop of *trans*-3-octene was pipetted into a vial and diluted with some of the liquid product (1-octene). The GC spectra of unspiked liquid product sample and the spiked sample were overlayed and the *trans*-3-octene peak was identified by the increase in peak height, although a very small increase was observed in this case (Figure 7.4).

*Trans-4-octene added to unspiked reaction product sample*

A drop of *trans*-4-octene was pipetted into a vial and diluted with some of the liquid product (1-octene). The GC spectra of unspiked liquid product sample and the spiked sample were overlayed and the *trans*-4-octene peak was identified by the increase in peak height (Figure 7.5).

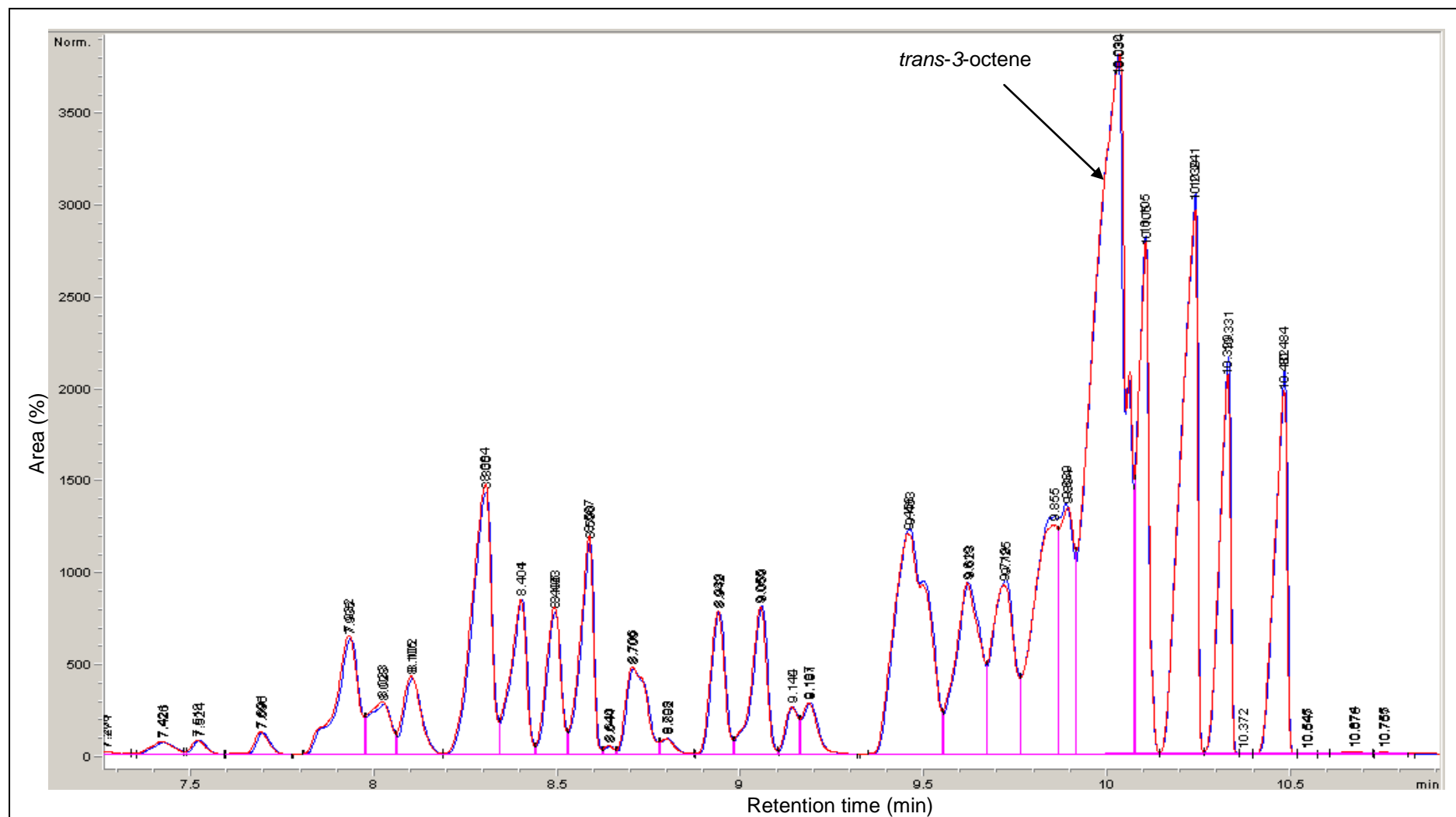


Figure 7.4: *Trans*-3-octene added to unspiked reaction product sample

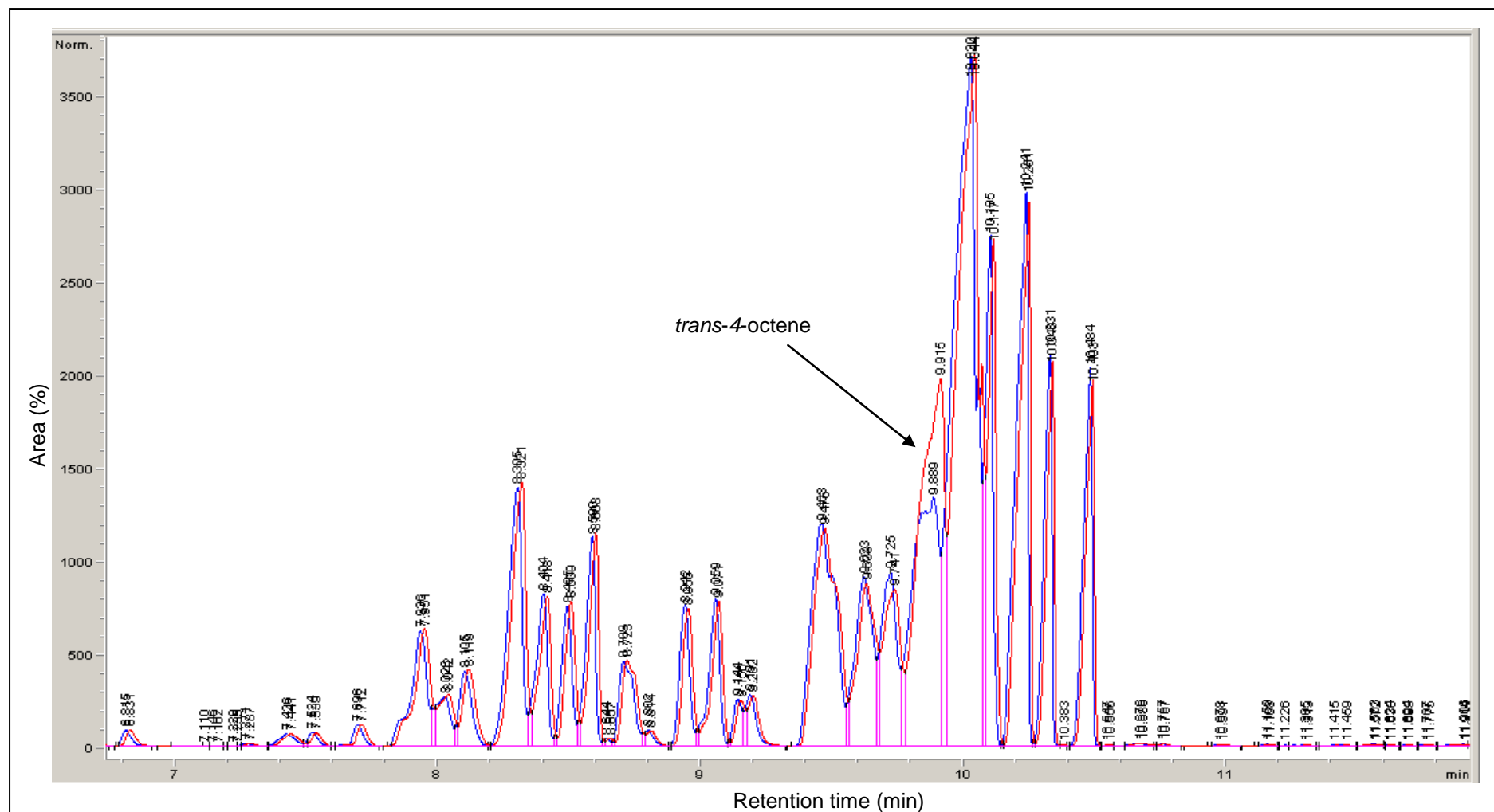


Figure 7.5: *Trans*-4-octene added to unspiked reaction product sample

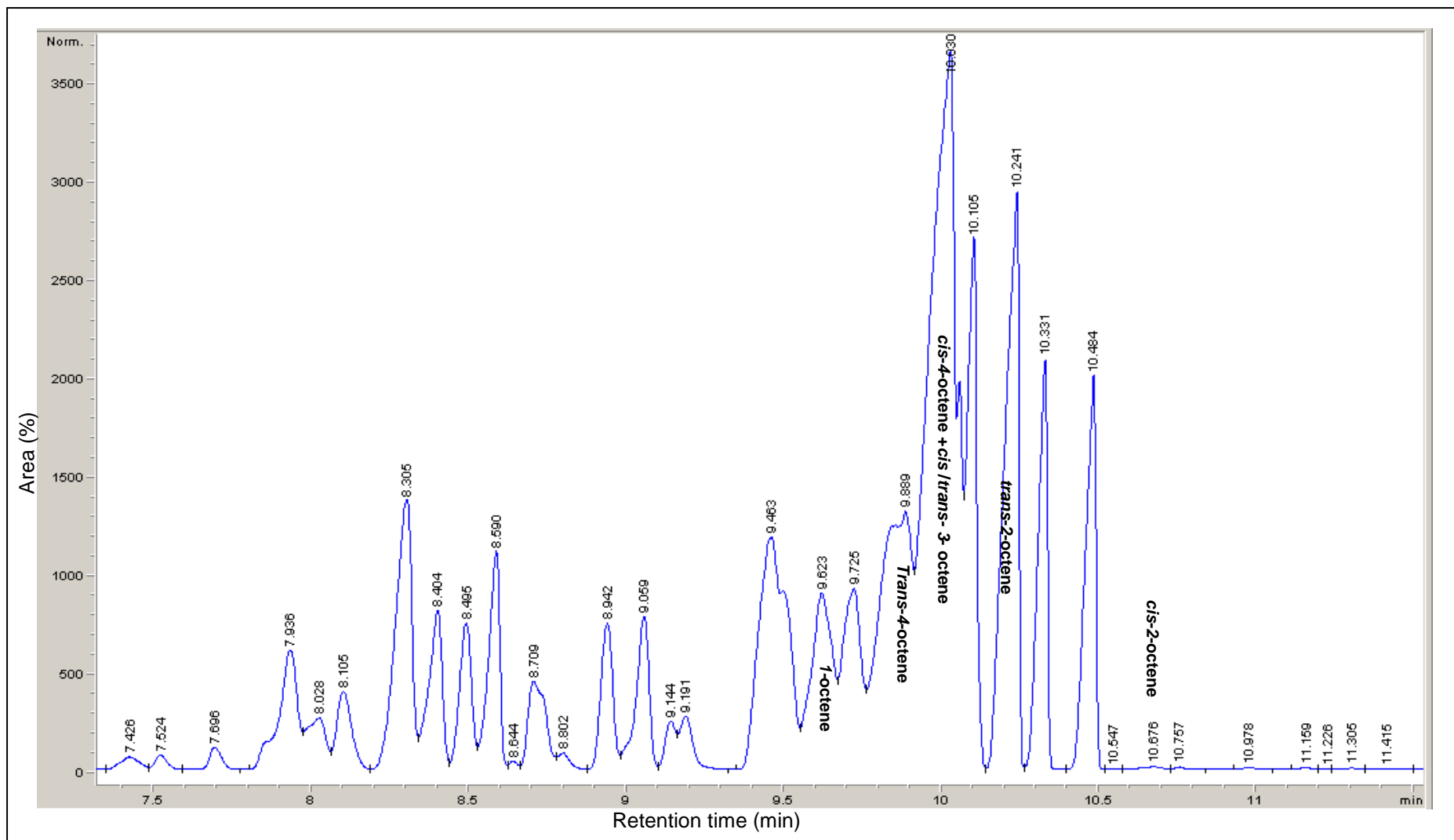


Figure 7.6: Identification of compounds with their respective retention times (min) as calculated (Table 7.1)



## 7.2 Kováts indices and retention time calculations

Kováts indices were used to determine the retention times of *cis* 2-, *cis* 3-, and *cis*-4-octene since the retention times for these compounds were unclear.

The formula used to calculate retention indices are [Kováts, 1958]:

$$I = 100 \times \left( n + (N-n) \frac{\log(t'_{r(\text{unknown})}) - \log(t'_{r(n)})}{\log(t'_{r(N)}) - \log(t'_{r(n)})} \right)$$

Where;

$I$  = Kováts retention index,

$n$  = the number of carbon atoms in the smaller  $n$ -alkane,

$N$  = the number of carbon atoms in the larger  $n$ -alkane,

$t'r$  = the adjusted retention time

To evaluate this calculation, experimentally determined retention times of *trans*-3-octene and *trans*-4-octene can be compared to the retention times calculated using the given formula. The results, in good agreement, are shown in Table 7.1.

Table 7.1			
Calculated retention times (min)			
Compound	Retention Index	Retention Time (min) from GC	Calculated retention time (min)
1-octene	786.8	9.623	-
<i>trans</i> -2-octene	801	10.24	-
<i>cis</i> -2-octene	810.2	-	10.64
<i>trans</i> -3-octene	796.5	10.030	10.043
<i>cis</i> -3-octene	798.4	-	10.030
<i>trans</i> -4-octene	795.2	9.889	9.983
<i>cis</i> -4-octene	797.9	-	10.105

The identification (and retention times) of peaks on the GC spectra of the compounds listed in Table 7.1 is given in Figure 7.6 and these will be used throughout this Chapter where needed to identify the products from the reactions of 1-octene.

### 7.3 1-Octene reacted over Eta alumina catalyst

#### *Conversion of 1-octene*

The conversion of 1-octene over the Eta alumina catalyst indicated that most of the 1-octene was converted at all three temperatures. Conversions between 94% and 100% were achieved.

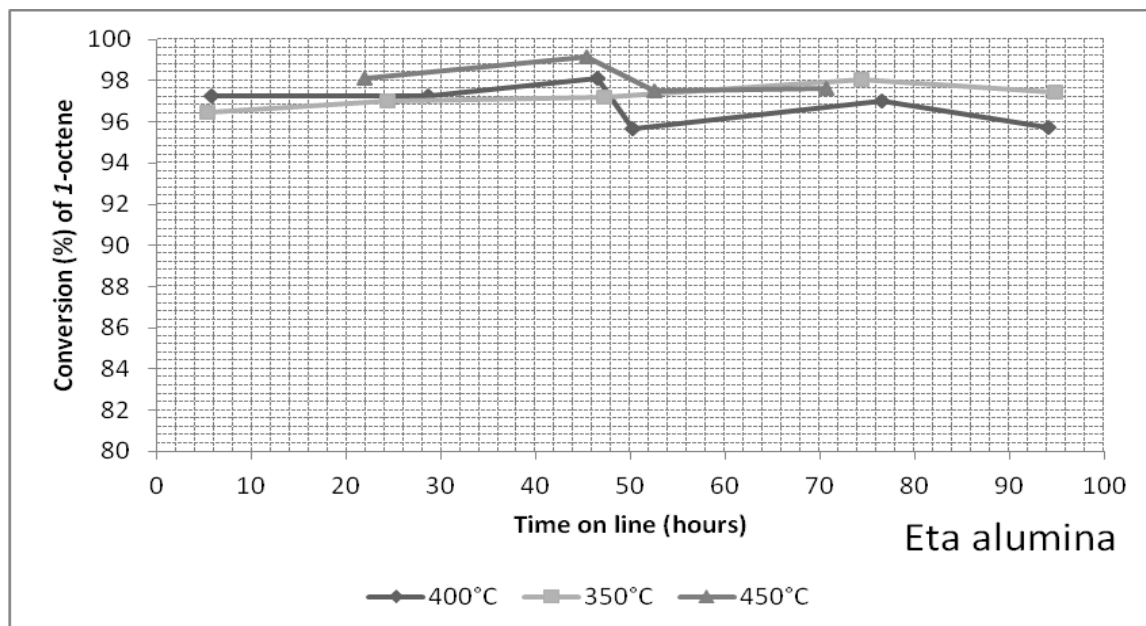


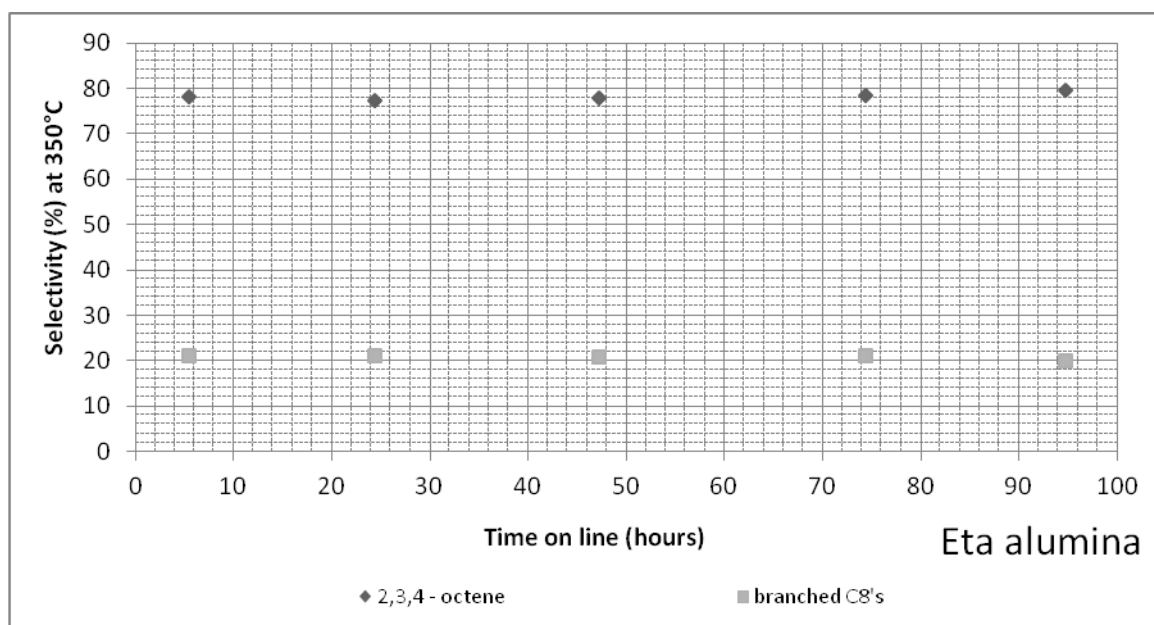
Figure 7.7: Conversion of 1-octene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Eta alumina catalyst

#### *Thermodynamic equilibrium*

No simulation was done on the isomers of octene. Octene consist of numerous isomers, making the simulation of thermodynamic equilibrium impractical.

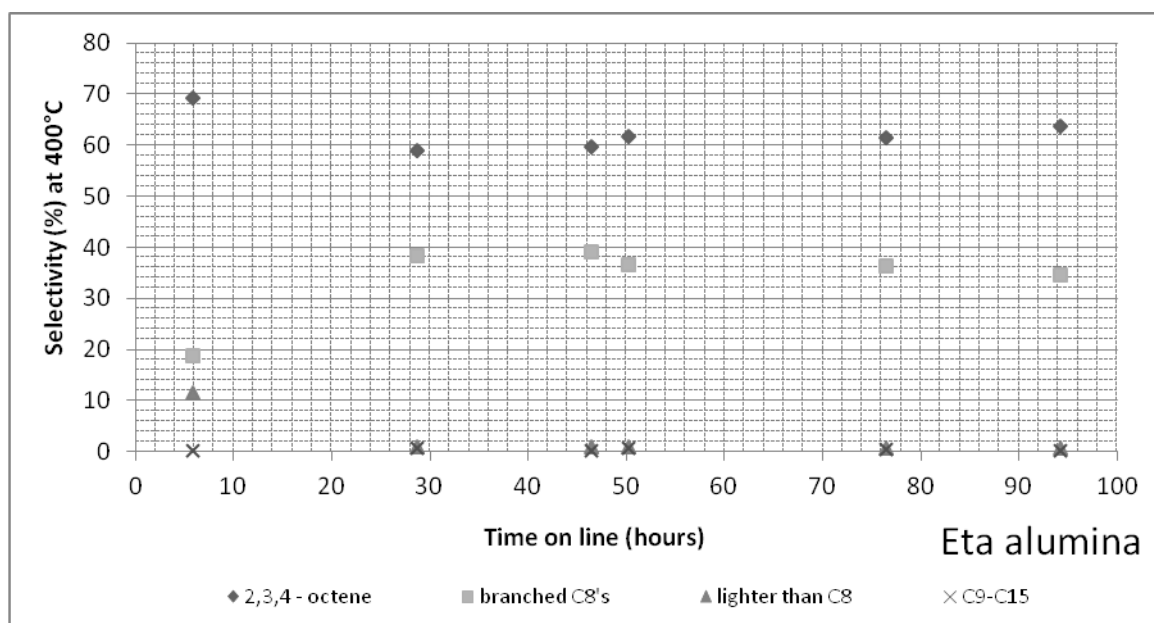
#### *Selectivity of 1-octene*

At 350 °C, a selectivity of 20% was reached towards branched C<sub>8</sub>s. Almost 80% of 2,3,4-octene was formed which is indicative of double bond shifts. Little to none of the compounds of fewer than C<sub>8</sub> as well as those from C<sub>9</sub>-C<sub>11</sub> occurred (Figure 7.8).



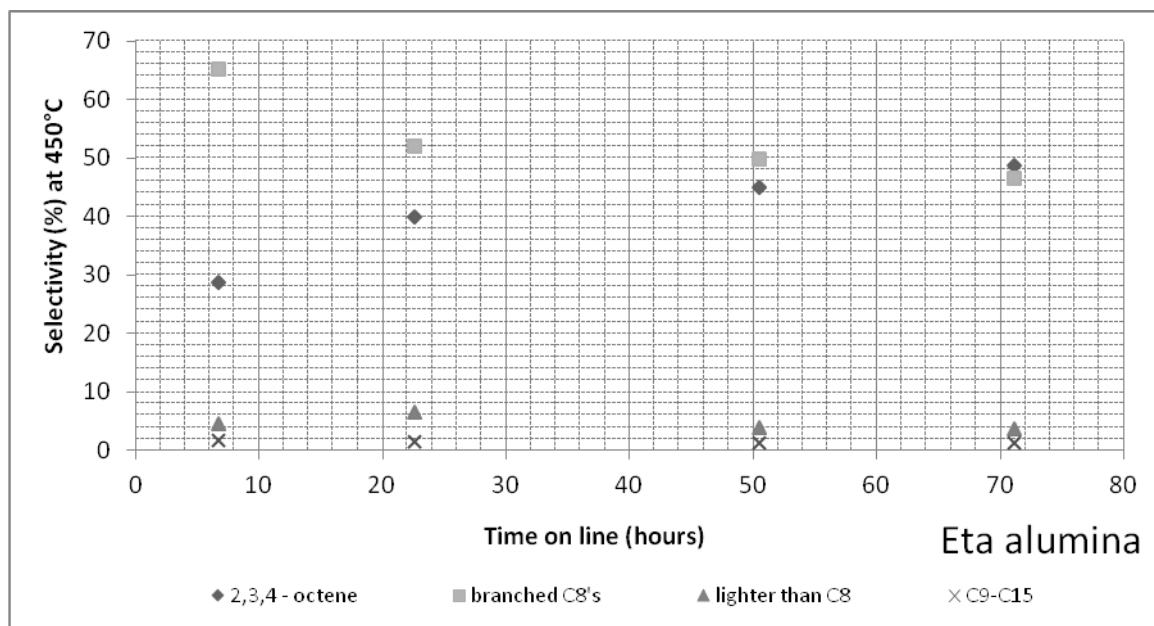
**Figure 7.8: Selectivity (%) of desired products obtained at 350 °C over the Eta alumina catalyst**

At 400 °C a selectivity between 60% and 70% of 2,3,4-octene was obtained. Yet again, this is indicative of double bond shifts. Fewer double bond shifts occurred at 400 °C than at 350 °C. More branched C<sub>8</sub> compounds formed at 400 °C than at 350 °C, (between 20%-40%) showing that more isomerization took place at the higher temperature and again little to no compounds of fewer than C<sub>8</sub> and between C<sub>9</sub>-C<sub>11</sub> formed at 400 °C (Figure 7.9).



**Figure 7.9: Selectivity (%) of desired products obtained at 400 °C over the Eta alumina catalyst**

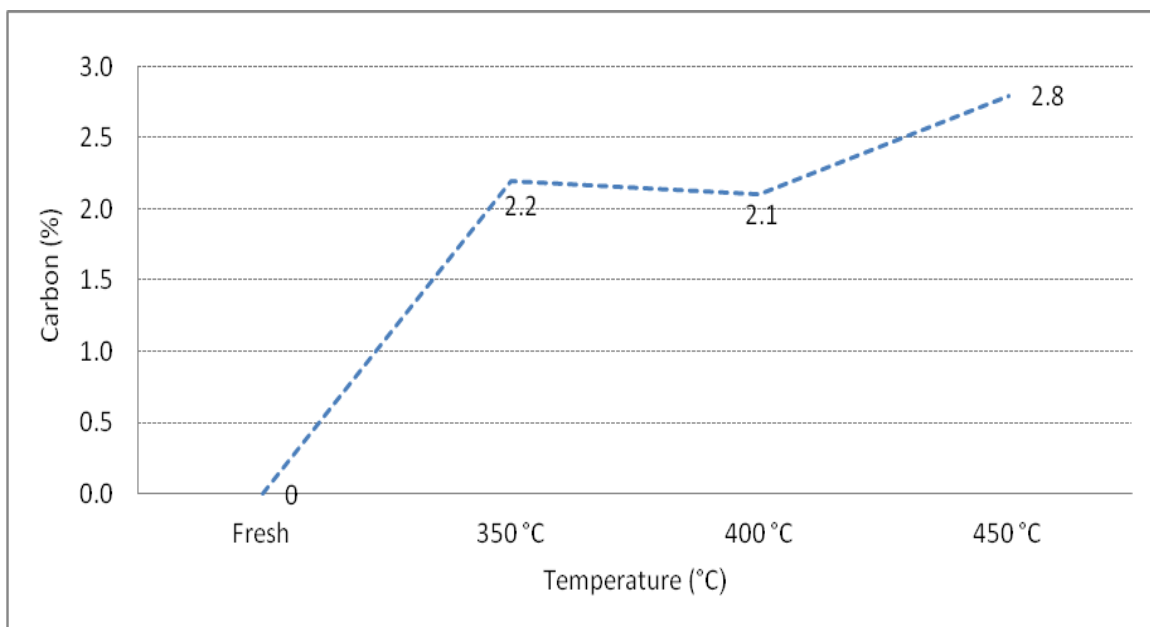
Isomerization occurred to the greatest extent at 450 °C, and a branched octene selectivity between 49% and 65% was obtained. The selectivity decreased with time on line. The lowest amount of 2,3,4-octenes formed at 450 °C. This is opposite to the trend observed for isomerization and indicates that the double bond shift reaction occurred less at 450 °C compared to the lower temperatures. Some lighter and heavier compounds formed at this temperature. Figure 7.10 demonstrates that the preferred temperature for isomerization of 1-octene over the Eta alumina catalyst is at 450 °C.



**Figure 7.10: Selectivity (%) of desired products obtained at 450 °C over the Eta alumina catalyst**

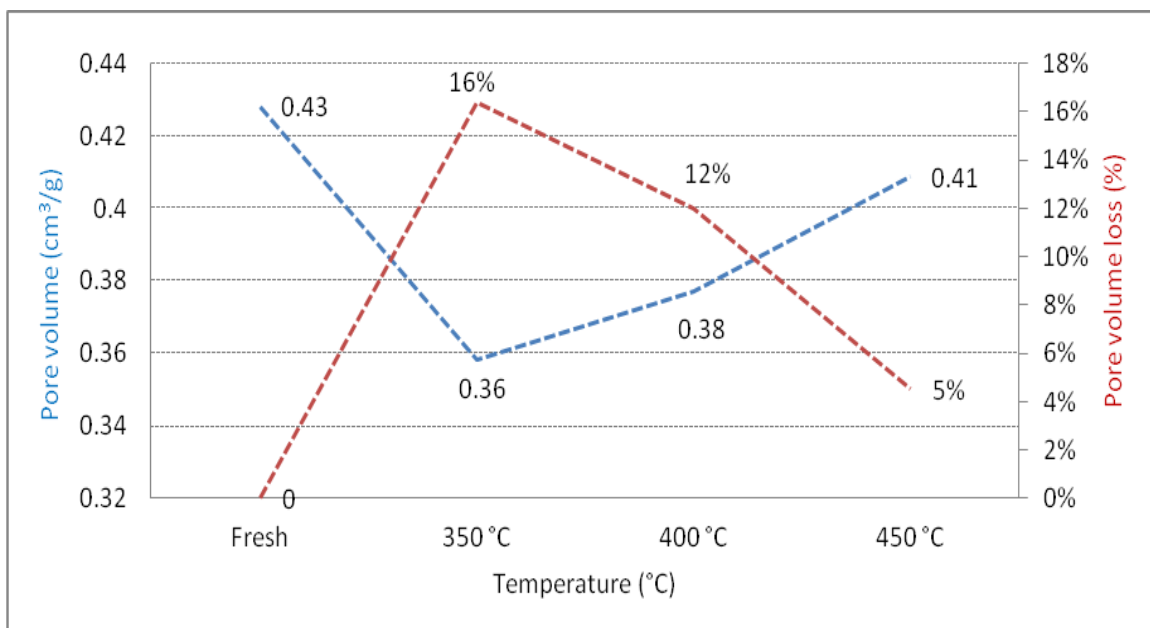
#### *Coking of the Eta alumina catalyst*

Figure 7.11 indicates an increase in the amount of fixed carbon deposited on the Eta alumina catalyst as the temperature increased.



**Figure 7.11: Carbon (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C**

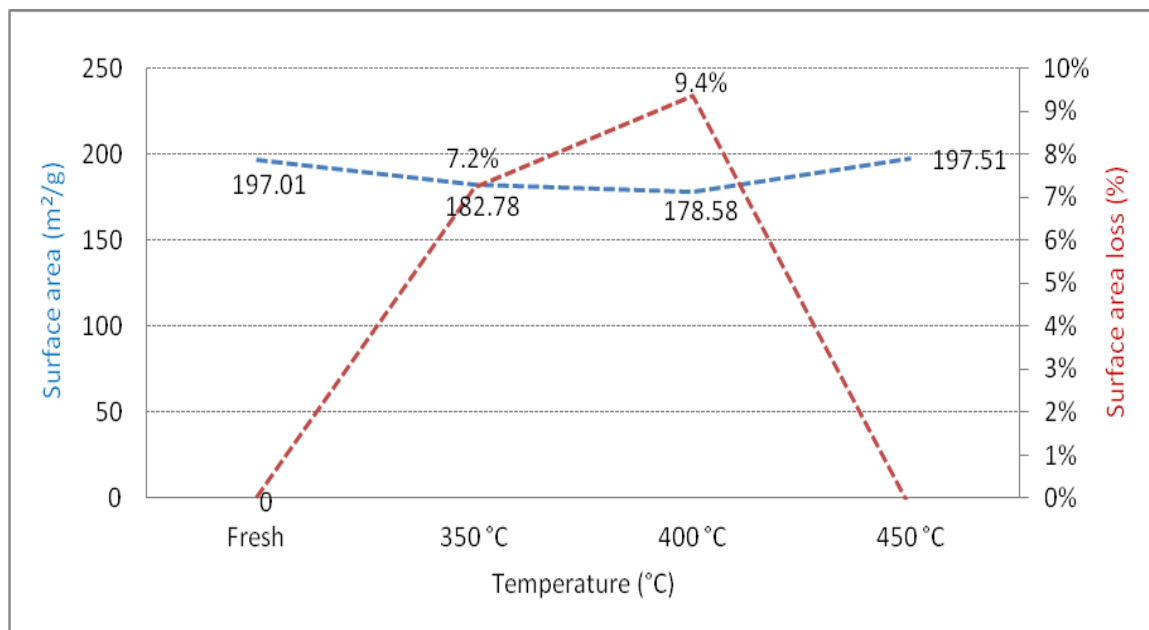
Contrary to the trends of the carbon results with temperature, Figure 7.12 indicates that the pore volume of the Eta alumina catalyst did not change much with temperature as only 5% of the pore volume was lost.



**Figure 7.12: Pore volume (cm³/g) of fresh Eta alumina and spent Eta alumina and pore volume loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C**

The percentage of surface area that was lost after the reaction of 1-octene over Eta alumina was low, and none of the surface area was lost at 450 °C. Although the amount of carbon (coke) deposited on the catalyst increased with an increase in temperature, no significant change occurred in the pore volume and surface

area of the catalyst. This indicates that the deposited carbon did not have an effect on these physical properties of the Eta alumina catalyst.

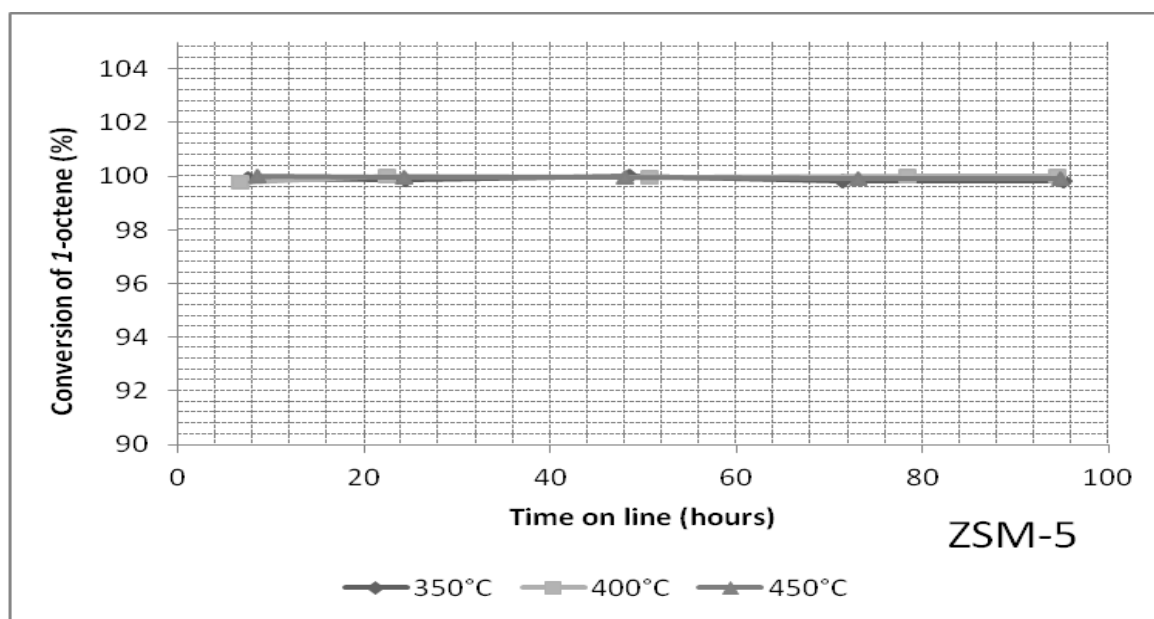


**Figure 7.13: Surface area (m<sup>2</sup>/g) of fresh Eta alumina and spent Eta alumina and surface area loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C**

#### 7.4 1-Octene reacted over ZSM-5 catalyst

##### *Conversion of 1-octene*

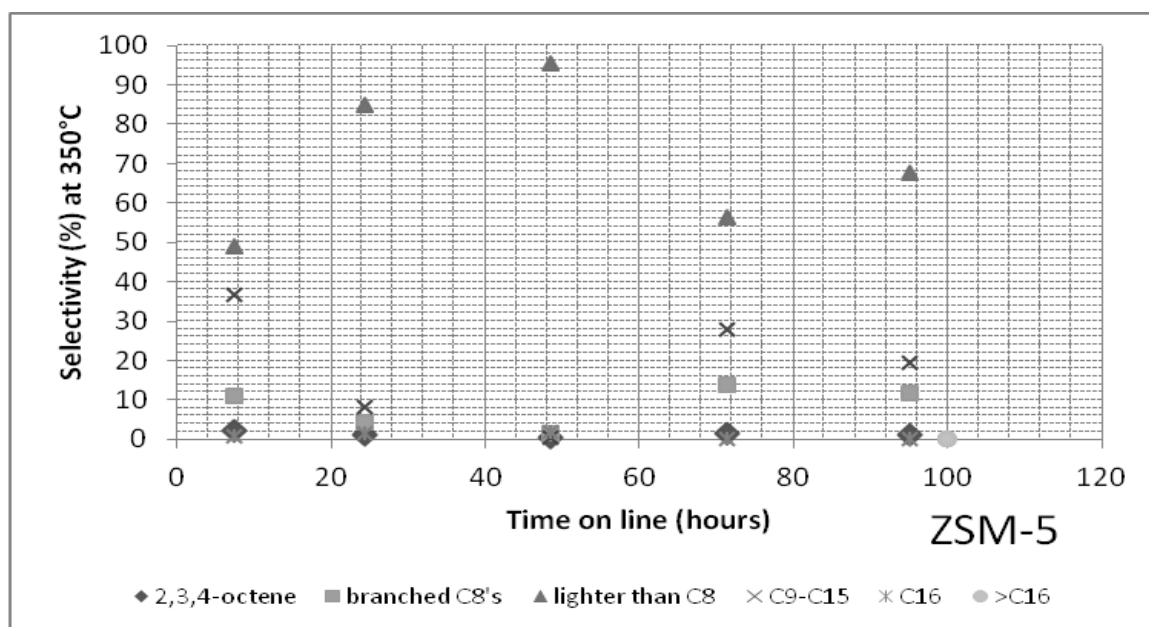
The conversion of 1-octene over the ZSM-5 catalyst indicated that all of the 1-octene was converted at all three temperatures (Figure 7.14).



**Figure 7.14: Conversion of 1-octene (%) after reaction at temperatures of 350°C, 400°C and 450°C obtained over the ZSM-5 catalyst**

### Selectivity of 1-octene

When reacting 1-octene over the ZSM-5 catalyst at 350 °C, cracking occurred to a large extent: 50%-90% of compounds lighter than C<sub>8</sub> formed. No double bond shift products were formed and only ±10% of branched C<sub>8</sub> compounds were observed. Oligomerization could be observed with the formation of the C<sub>9</sub>-C<sub>15</sub> products (Figure 7.15).



**Figure 7.15: Selectivity (%) of desired products obtained at 350 °C over the ZSM-5 catalyst**

At 400 °C the formation of branched C<sub>8</sub> compounds were low which indicates that little isomerization took place when contacting 1-octene over the ZSM-5 catalyst. Little to none of the 2,3,4-octene formed which shows that very few double bond shift reactions occurred. Compounds lighter than C<sub>8</sub> formed and showed that high amounts of cracking occurred with time on line. The C<sub>9</sub>-C<sub>15</sub> products that formed indicated that oligomerization occurred. The formation of any other products were negligible (Figure 7.16).

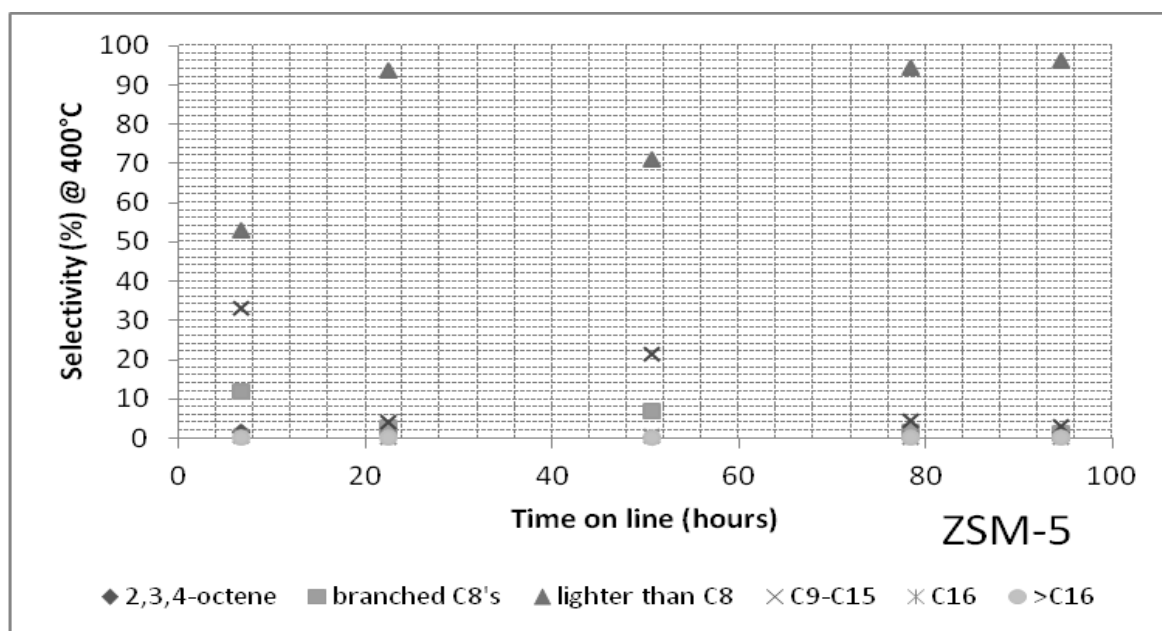


Figure 7.16: Selectivity (%) of desired products obtained at 400 °C over the ZSM-5 catalyst

At 450 °C, cracking was the major reaction that occurred when 1-octene was contacted over the ZSM-5 catalyst and between 60% and 85% of compounds lighter than C<sub>8</sub> was formed. Little isomerization took place as only approximately 0%-20% of branched C<sub>8</sub> compounds formed. 20%-30% of C<sub>9</sub>-C<sub>15</sub> compounds formed which is indicative of some oligomerization reactions taking place (Figure 7.17).

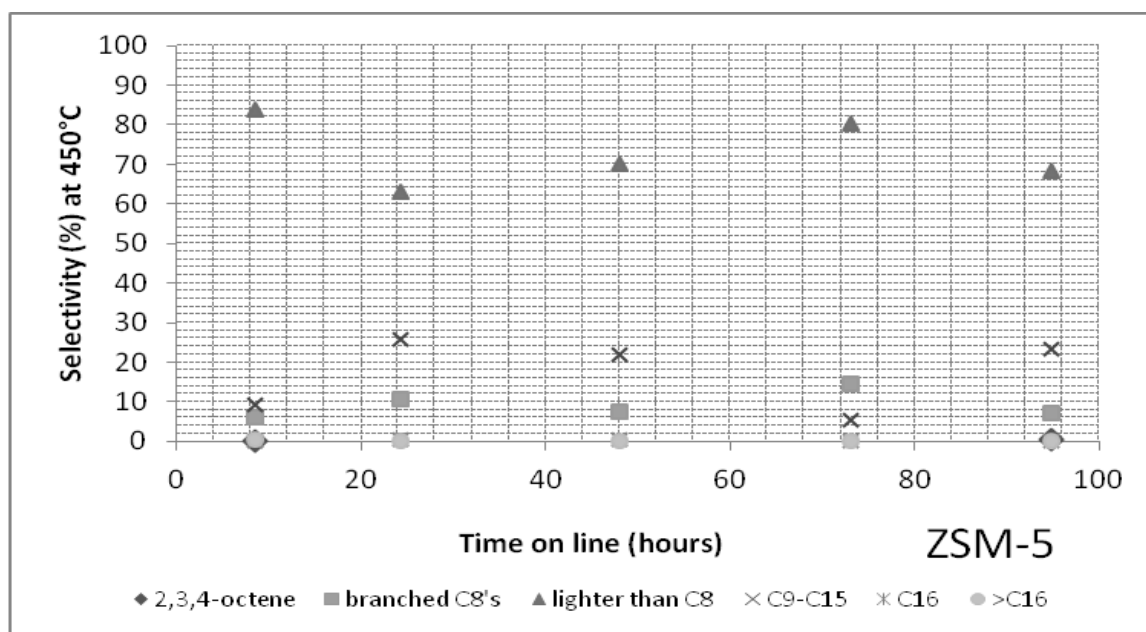


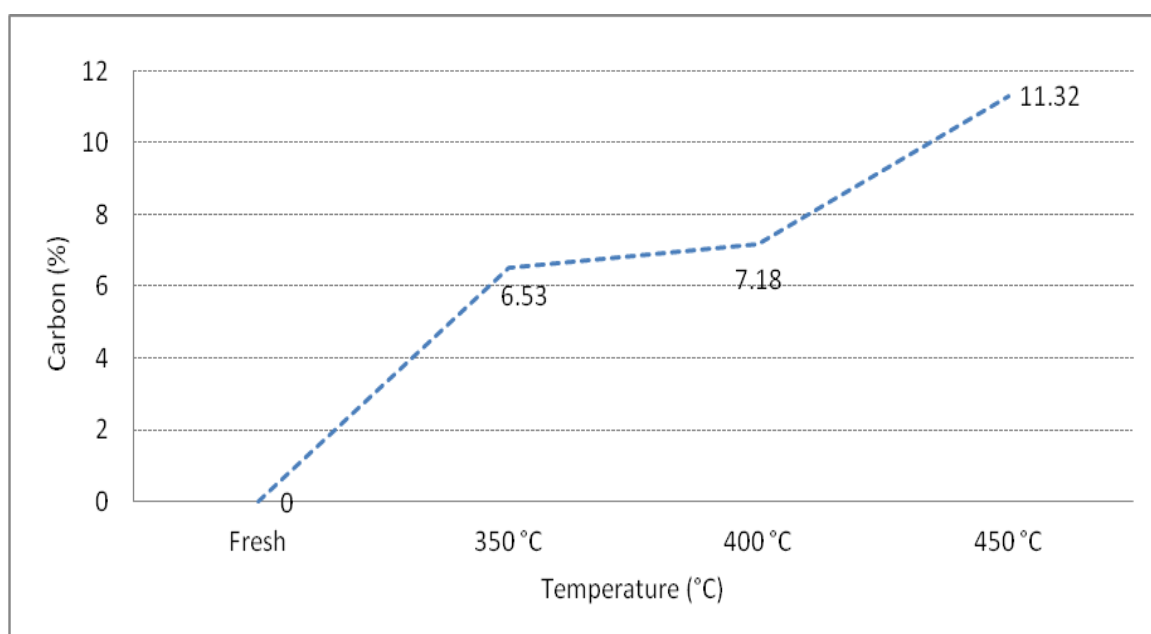
Figure 7.17: Selectivity (%) of desired products obtained at 450 °C over the ZSM-5 catalyst



From Figure 7.15, 7.16 and 7.17, it is evident that very little isomerization occurred at all three experimental temperatures. However, it is important to keep in mind that C<sub>8</sub> isomers (branched C<sub>8</sub>s) may have formed and just cracked after they were formed. Cracking occurred at all three temperatures which can be seen from the production of the products lighter than C<sub>8</sub>. Smaller amounts of the other products were formed. ZSM-5 is not a preferred catalyst for skeletal isomerization of 1-octene.

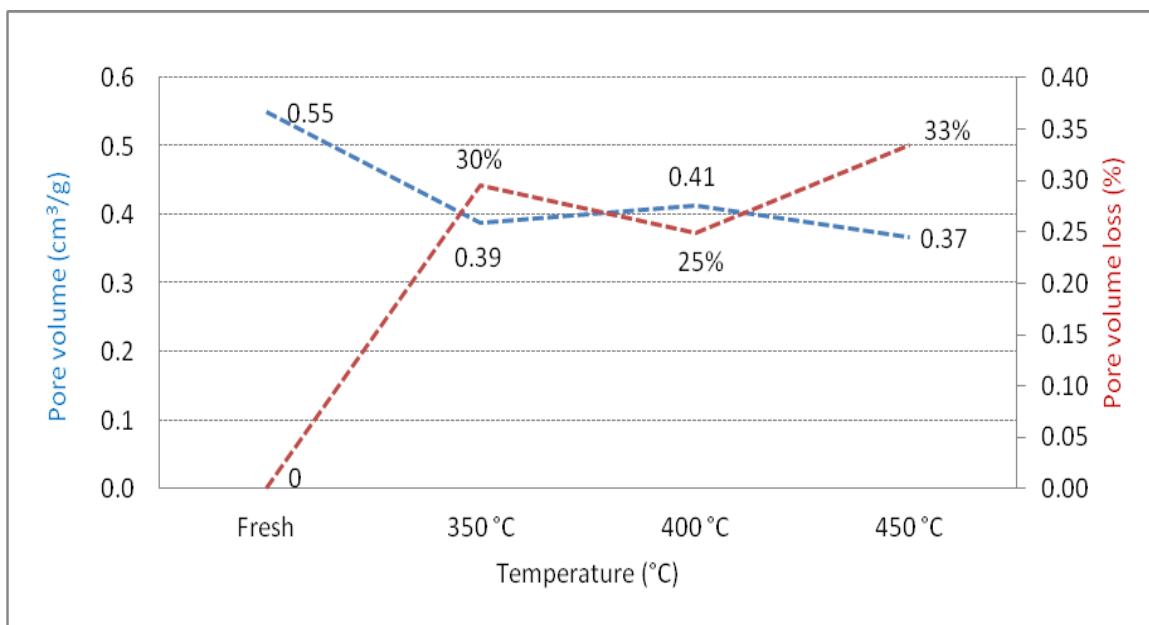
#### *Coking of the ZSM-5 catalyst*

An increase in the amount of fixed carbon deposited on the ZSM-5 catalyst as the temperature increased was observed as represented in Figure 7.18.



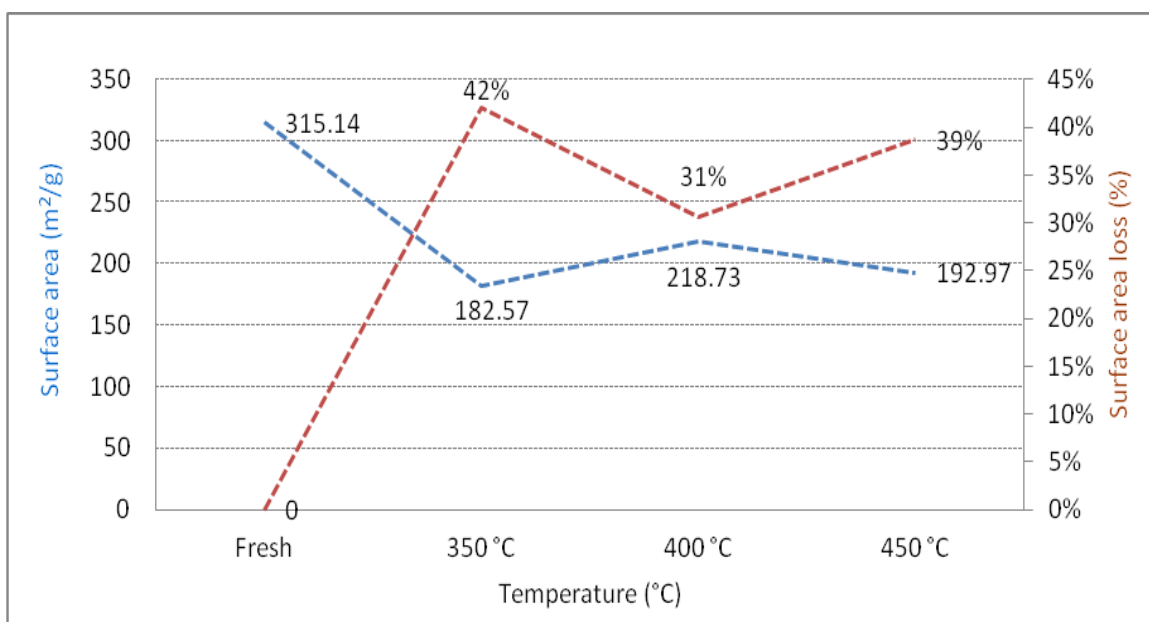
**Figure 7.18: Carbon (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350°C, 400°C and 450°C**

There was almost no change in the pore volume of the ZSM-5 catalyst (Figure 7.19). At 350 °C the pore volume was 0.39 cm<sup>3</sup>/g and at 450 °C the pore volume was 0.37 cm<sup>3</sup>/g. Thus only 3% of the pore volume was lost between the lowest and the highest temperature which showed that even though some coke formed as shown in Figure 7.18, it did not have a noticeable effect on the pore volume of the ZSM-5 catalyst.



**Figure 7.19: Pore volume (cm<sup>3</sup>/g) of fresh ZSM-5 and spent ZSM-5 and pore volume loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C**

A decrease in surface area was also observed between the fresh catalyst and the exposed catalysts at the various temperatures. Considering all three temperatures, the surface area of the ZSM-5 catalyst seemed to stabilize and little loss of surface area on the ZSM-5 catalyst between the three temperatures was observed.

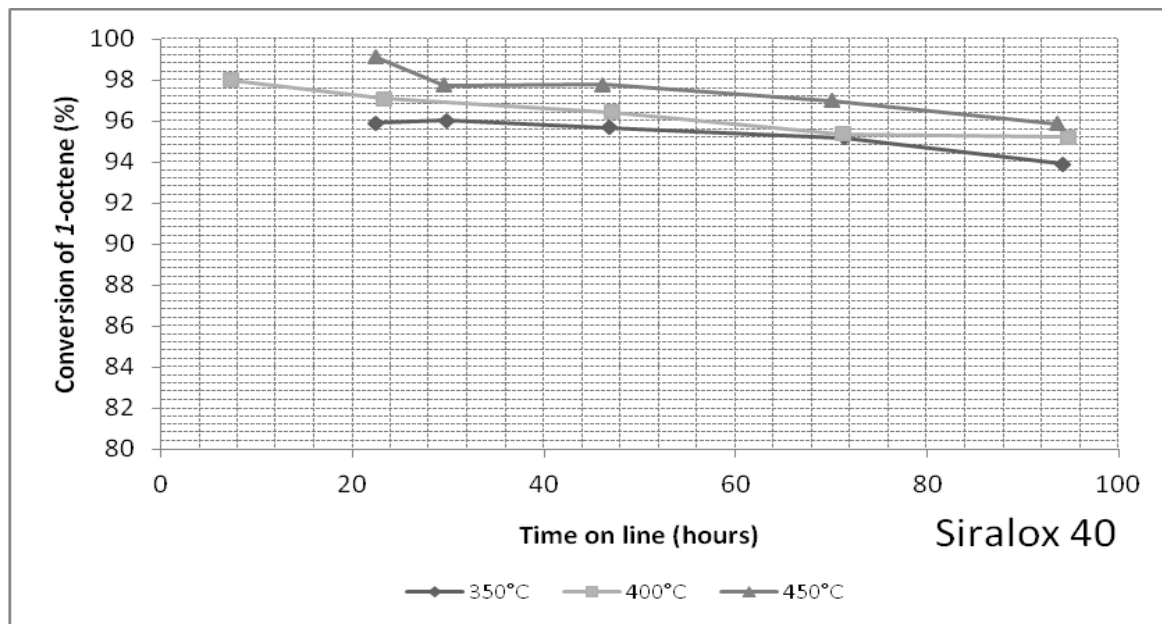


**Figure 7.20: Surface area (m<sup>2</sup>/g) of fresh ZSM-5 and spent ZSM-5 and surface area loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C**

## 7.5 1-Octene reacted over Siralox 40 catalyst

### Conversion of 1-octene

The conversion of 1-octene over the Siralox 40 catalyst indicated that most of the 1-octene was converted at all three temperatures (Figure 7.21). A conversion around 95% to almost 100% was achieved.



**Figure 7.21: Conversion of 1-octene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst**

### Selectivity of 1-octene

Reacting 1-octene over Siralox 40 at 350 °C indicated that isomerization occurred as can be seen from the formation of branched octenes, but as time on line increased, isomerization decreased. Simultaneously to isomerization, double bond shifts increases from 40% to 70% (as isomerization decreased). Less than 10% of the other products formed, which is indicative of no oligomerization and no cracking during this reaction at 350 °C (Figure 7.22).

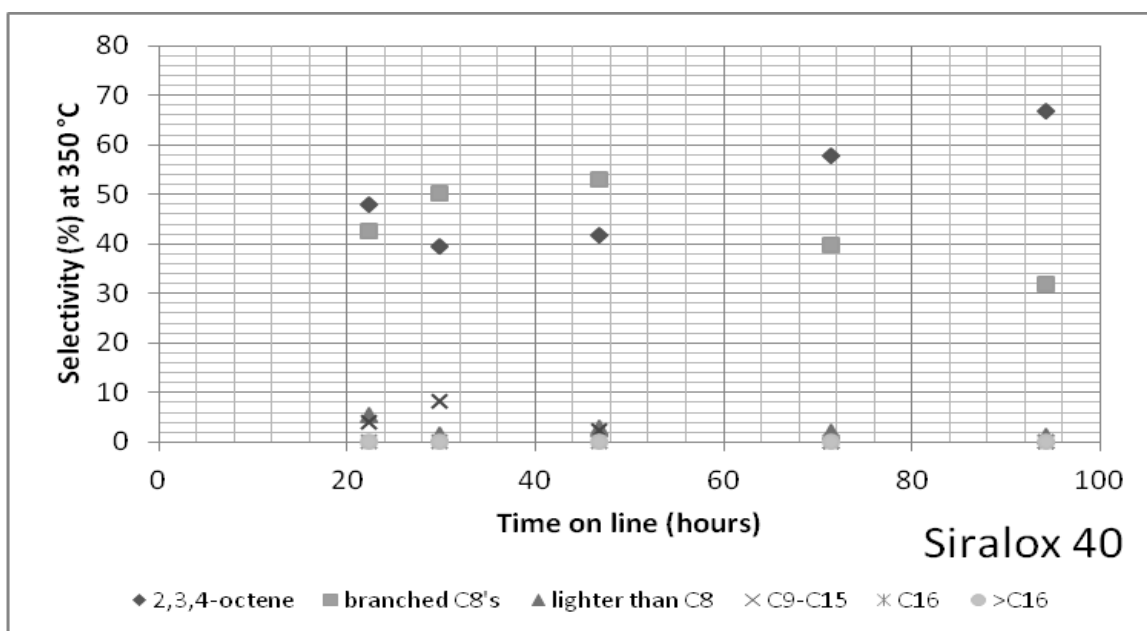


Figure 7.22: Selectivity (%) of desired products obtained at 350 °C over the Siralox 40 catalyst

At 400 °C the formation of branched C<sub>8</sub> was between 50% and 60% which indicates that isomerization took place when contacting 1-octene over the Siralox 40 catalyst. Similar to the reaction at 350 °C, an increase in double bond shift occurred with a decrease in the isomerization. A decline in cracking was observed and little to none of the heavier products formed (Figure 7.23).

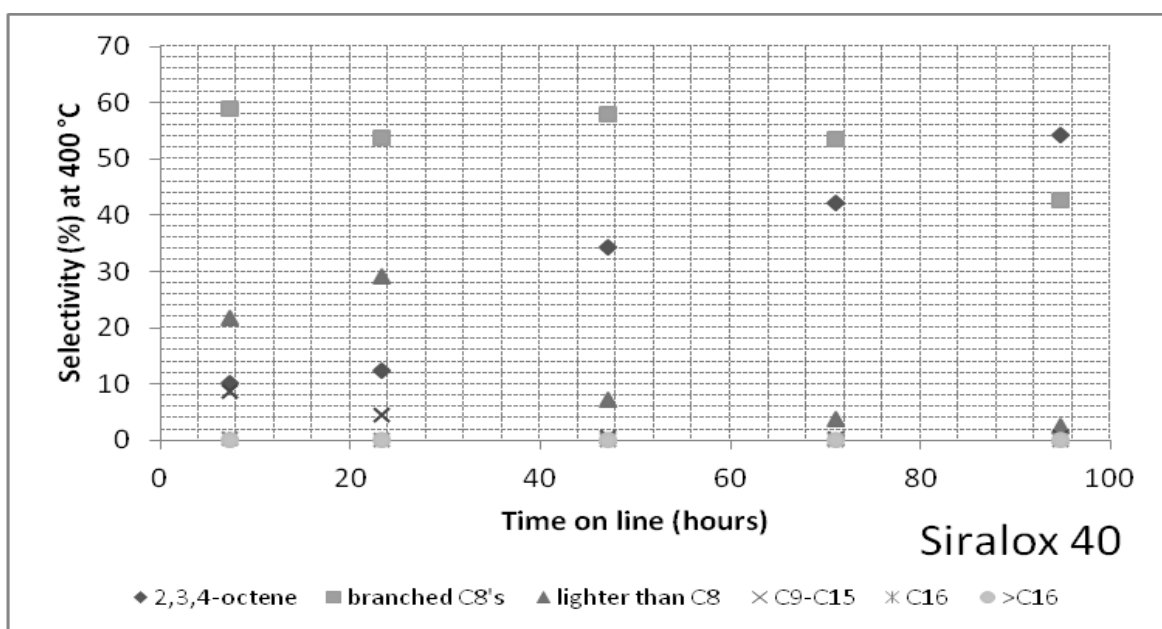
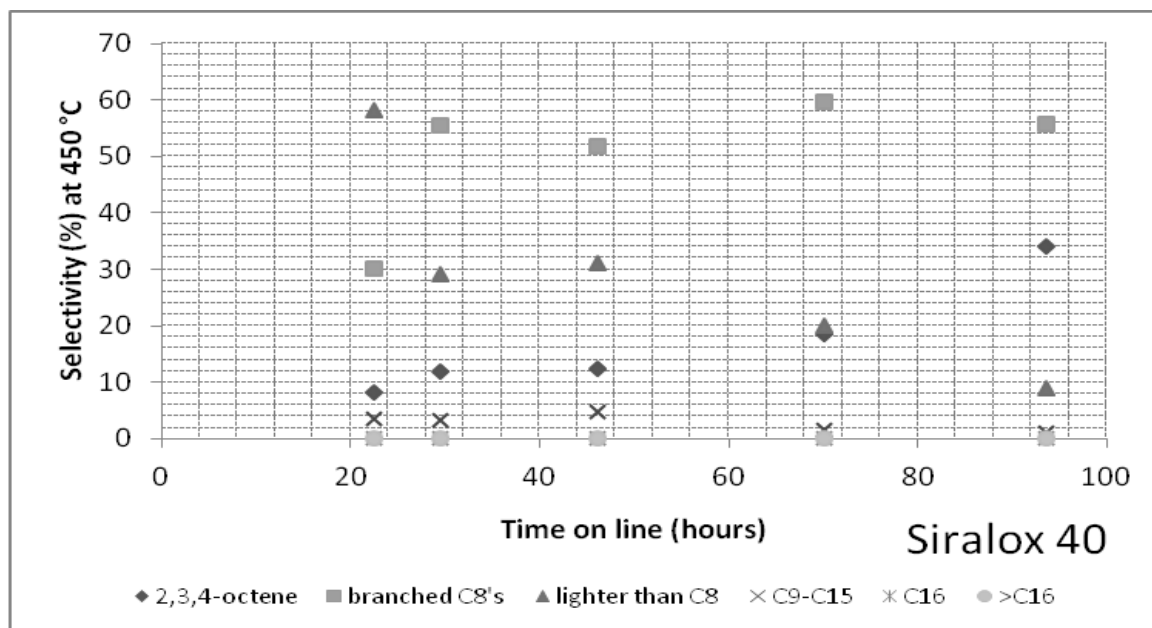


Figure 7.23: Selectivity (%) of desired products obtained at 400 °C over the Siralox 40 catalyst

As with the reaction of 1-octene over Siralox 40 at 400 °C, the reaction of 1-octene over Siralox 40 at 450 °C also resulted in the formation of 50%-60% branched octenes which is indicative of isomerization. An increase in double bond shifts was observed with time. Lots of cracking (formation of compounds lighter than C<sub>8</sub>)

also occurred and soon thereafter it declined with time on line. Oligomerization took place which can be seen from 10% C<sub>9</sub>-C<sub>15</sub> compounds that formed and the presence of very small amounts of the heavier compounds in the product mixtures (Figure 7.24).

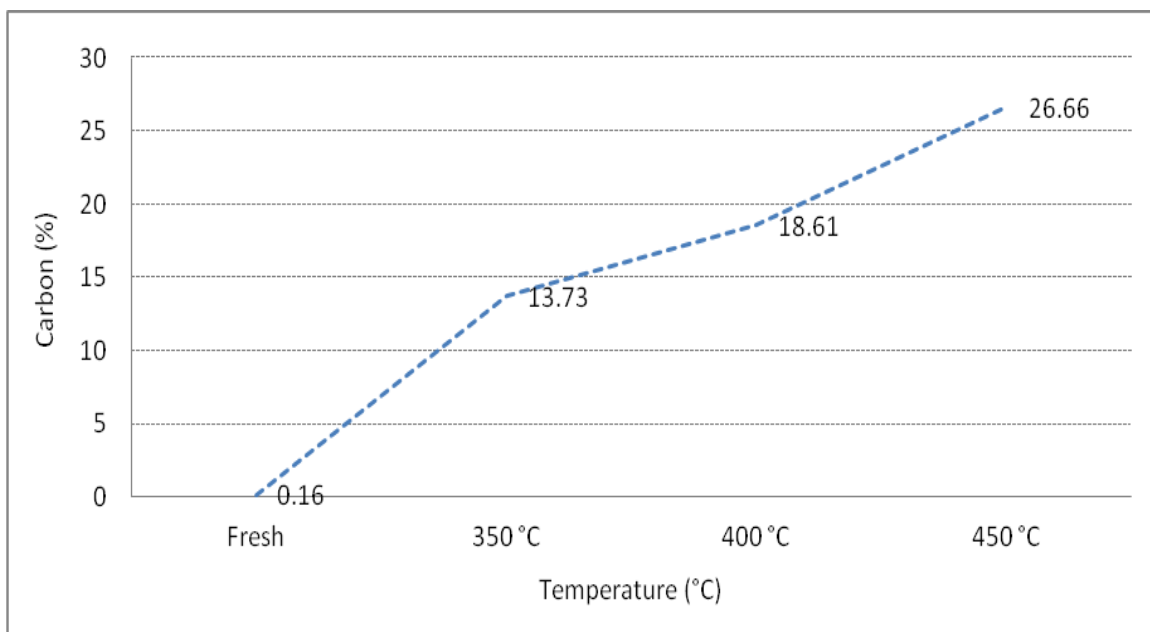


**Figure 7.24: Selectivity (%) of desired products obtained at 450 °C over the Siralox 40 catalyst**

Figures 7.23 and 7.24 indicate that isomerization occurred at 400 °C and 450 °C, although contacting 1-octene over the Siralox 40 catalyst was only 50%-60% selective towards branched C<sub>8</sub> compounds.

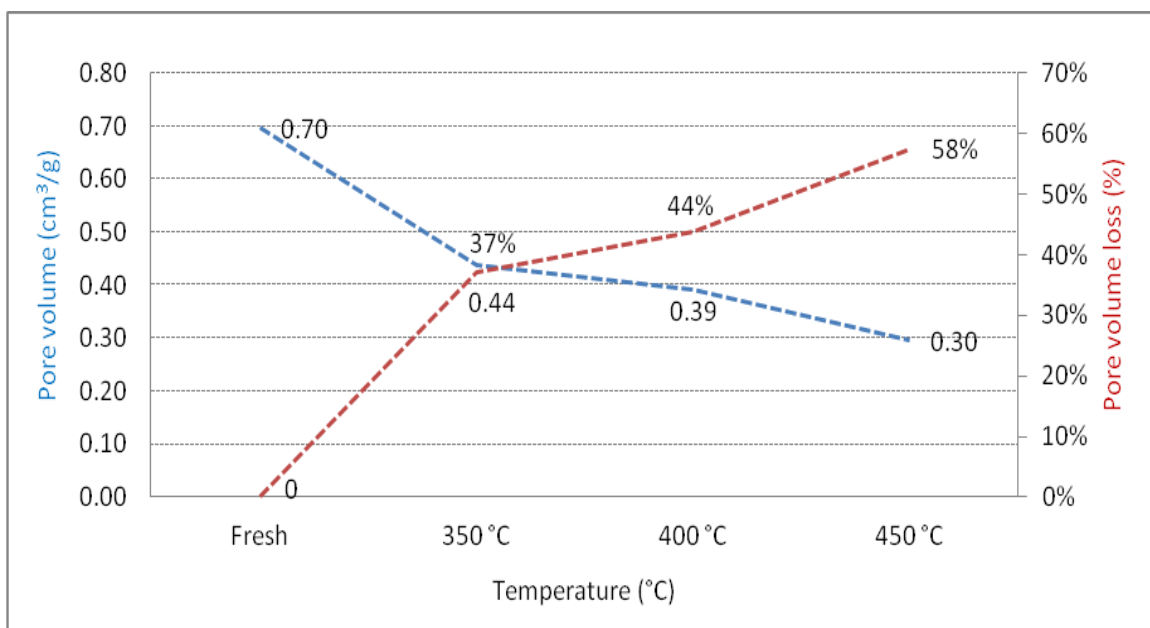
#### *Coking of the Siralox 40 catalyst*

Figure 7.25 indicates a gradual increase to approximately 27% in the amount of carbon deposited on the Siralox 40 catalyst as the temperature increased.



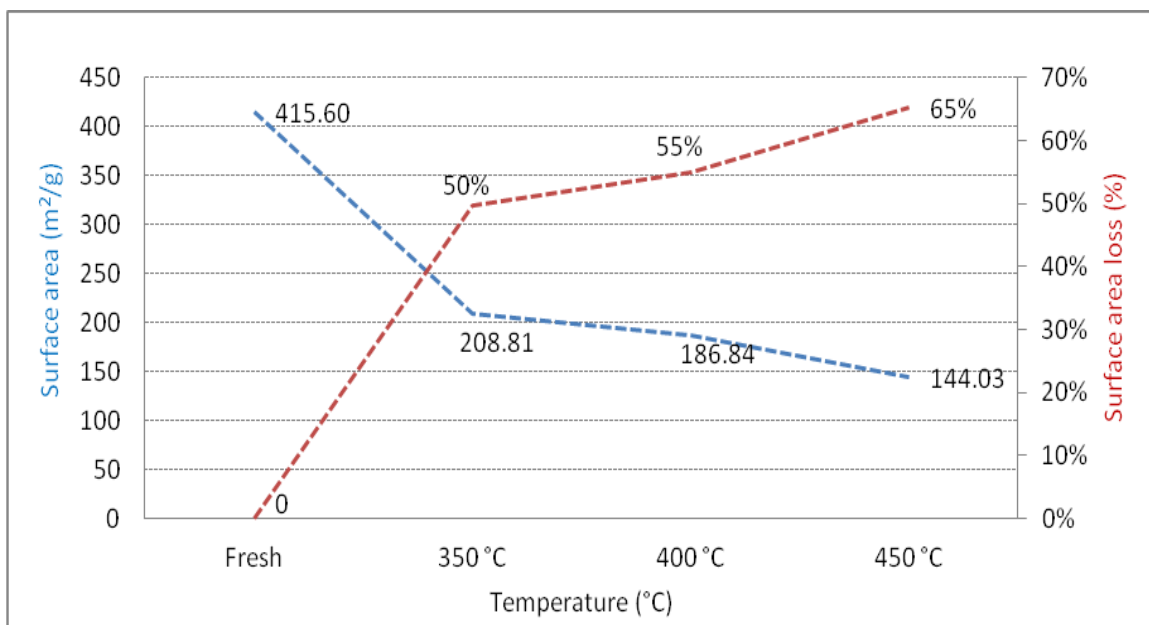
**Figure 7.25: Carbon (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C**

As the amount of carbon (coke) increased, the pore volume decreased and the catalyst lost 58% of its pore volume at 450 °C due to blockage of the Siralox 40 catalyst's pores (Figure 7.26).



**Figure 7.26: Pore volume (cm<sup>3</sup>/g) of fresh Siralox 40 and spent Siralox 40 and pore volume loss (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C**

Not surprisingly, as for the pore volumes, a decrease in surface areas was also observed with an increase in temperature. Reaching 450 °C the percentage loss in surface area (65%) and the percentage loss in pore volume (58%) were close to each other.

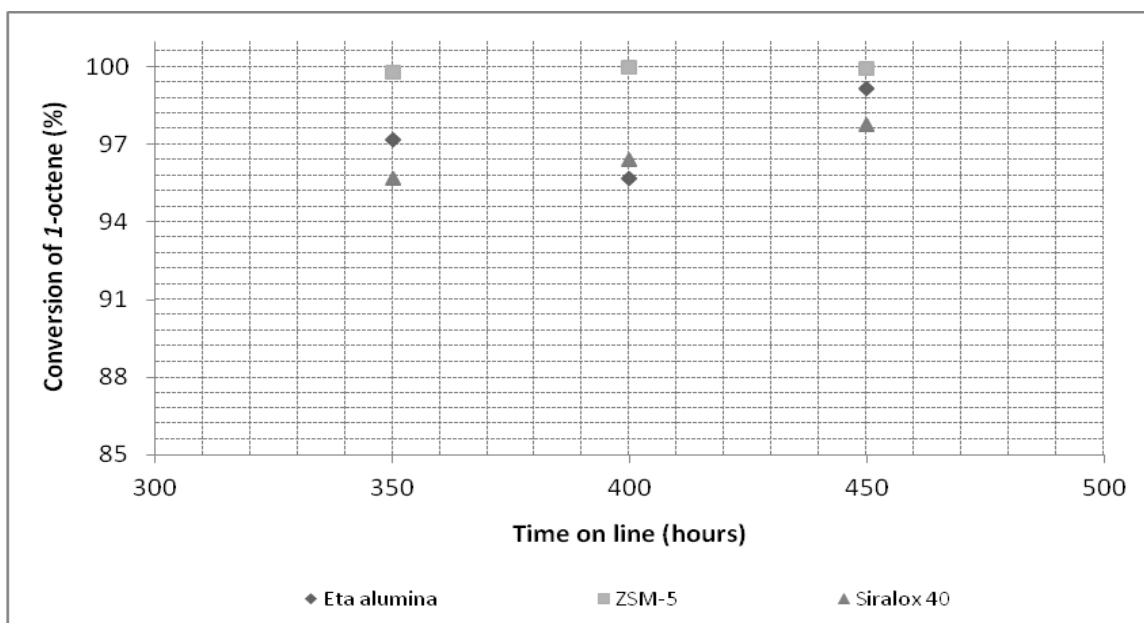


**Figure 7.27:** Surface area (m<sup>2</sup>/g) of fresh Siralox 40 and spent Siralox 40 and surface area loss (%) of fresh and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

## 7.6 Comparisons of the three catalysts

### *Conversion of 1-octene*

Figure 7.28 indicates that all three the catalysts used in the reaction with 1-octene converted almost all the 1-octene to various products. The conversion with all three catalyst at all three temperatures were above 95% and showed the high activity of all three catalysts when 1-octene is contacted with them.

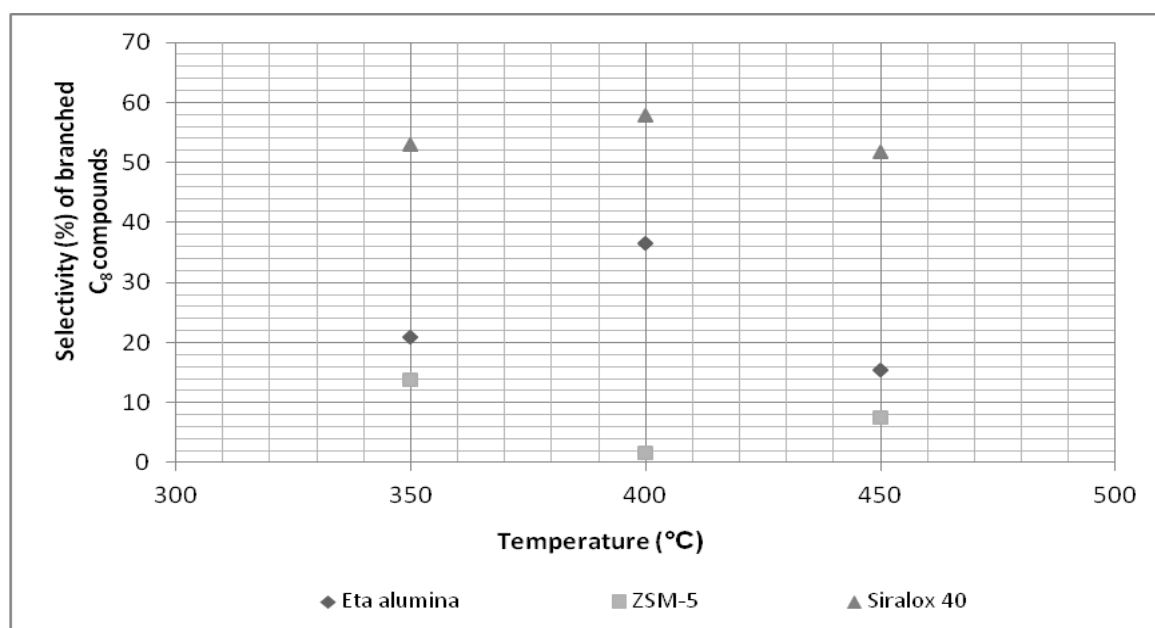


**Figure 7.28:** Conversion of 1-octene (%) at steady state after reaction at temperatures of 350 °C, 400 °C and 450 °C using the catalysts Eta alumina, ZSM-5 and Siralox 40

### Selectivity of 1-octene

Results were taken for each catalyst at steady state (Eta alumina catalyst between 45 and 51 hours on line, ZSM-5 catalyst between 48 and 79 hours on line and Siralox 40 catalyst between 23 and 47 hours on line). The main aim was to skeletally isomerize 1-octene. From Figure 7.29 it is evident that the catalysts which best skeletally isomerized 1-octene to its branched isomers were firstly Siralox 40, then Eta alumina and lastly ZSM-5. ZSM-5 is the catalyst which produced the least amount of branched C<sub>8</sub> compounds which makes ZSM-5 the least attractive catalyst of the three to use in the skeletal isomerization of 1-octene. Since the selectivity to branched C<sub>8</sub> compounds was below 50% when using the Eta alumina catalyst, the option for using this catalyst in skeletal isomerization of 1-octene is also eliminated. The Siralox 40 catalyst, however, is the only catalyst which produced branched C<sub>8</sub> compounds.

At all three experimental temperatures, between 50% and 60% selectivity towards the branched C<sub>8</sub> compounds was obtained.



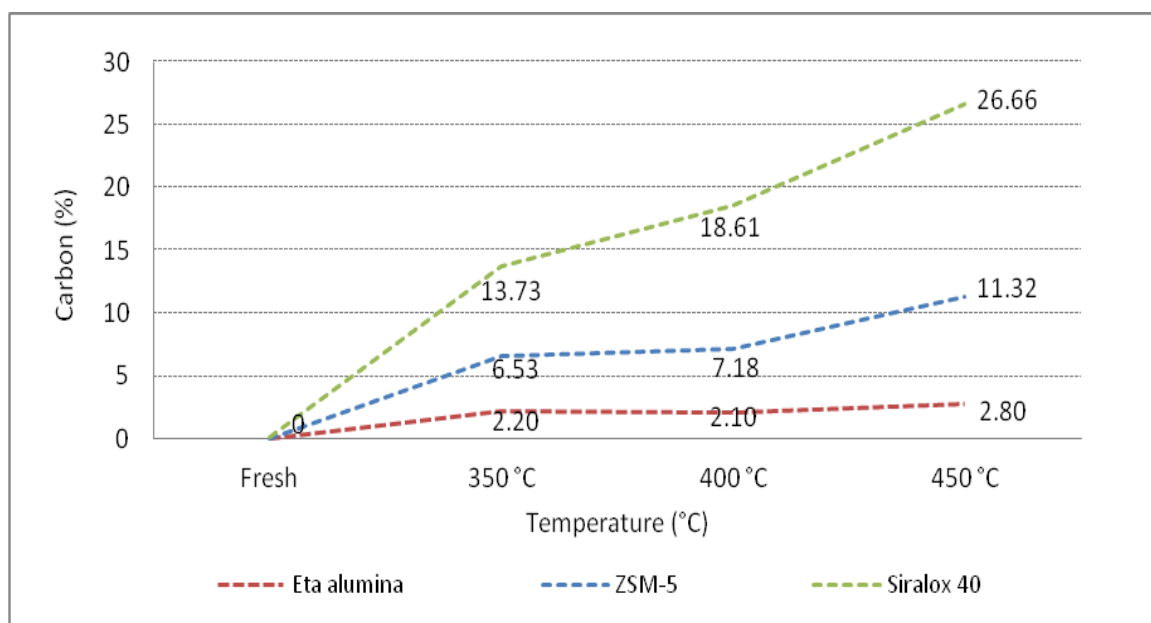
**Figure 7.29: Selectivity (%) obtained at steady state for each experimental run over the three catalysts at temperatures of 350 °C, 400 °C and 450 °C**

### Coking

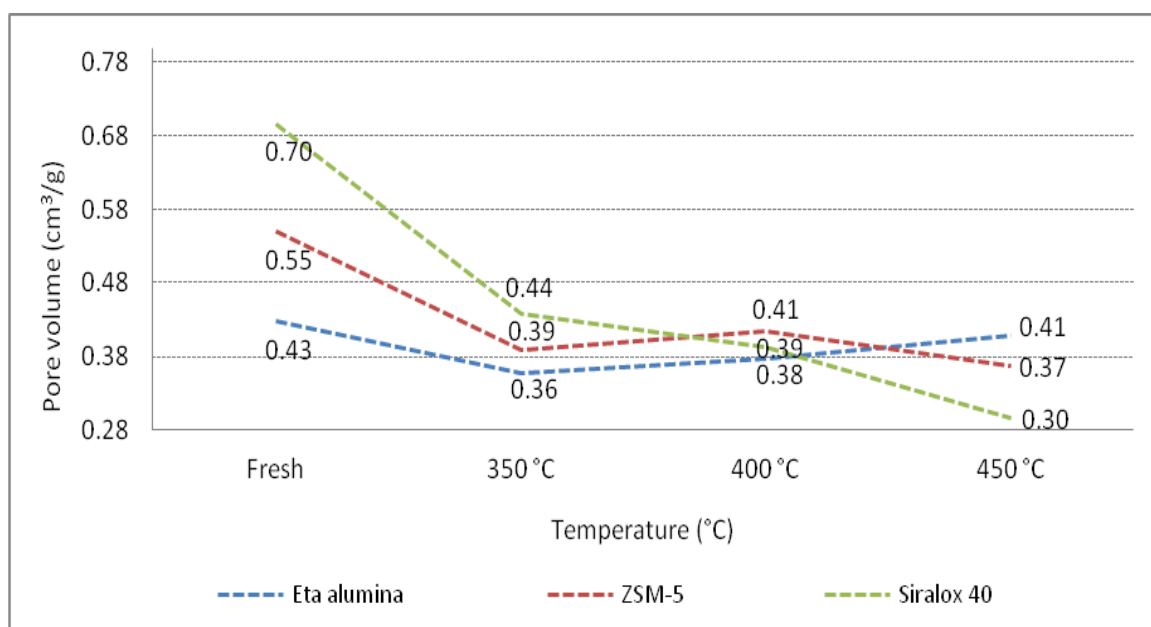
From Figure 7.30 and it can be seen that the Siralox 40 catalyst is the catalyst on which most carbon deposited as the temperature increased. With an increase in carbon content (coke), the pore volumes and surface areas of the catalysts (Figure 7.31 and 7.32) were reduced. When comparing Siralox 40 to the Eta alumina and ZSM-5, the Siralox 40 catalyst had the smallest remaining surface area and pore volume when reacted with 1-octene at 450 °C, thus after coking.



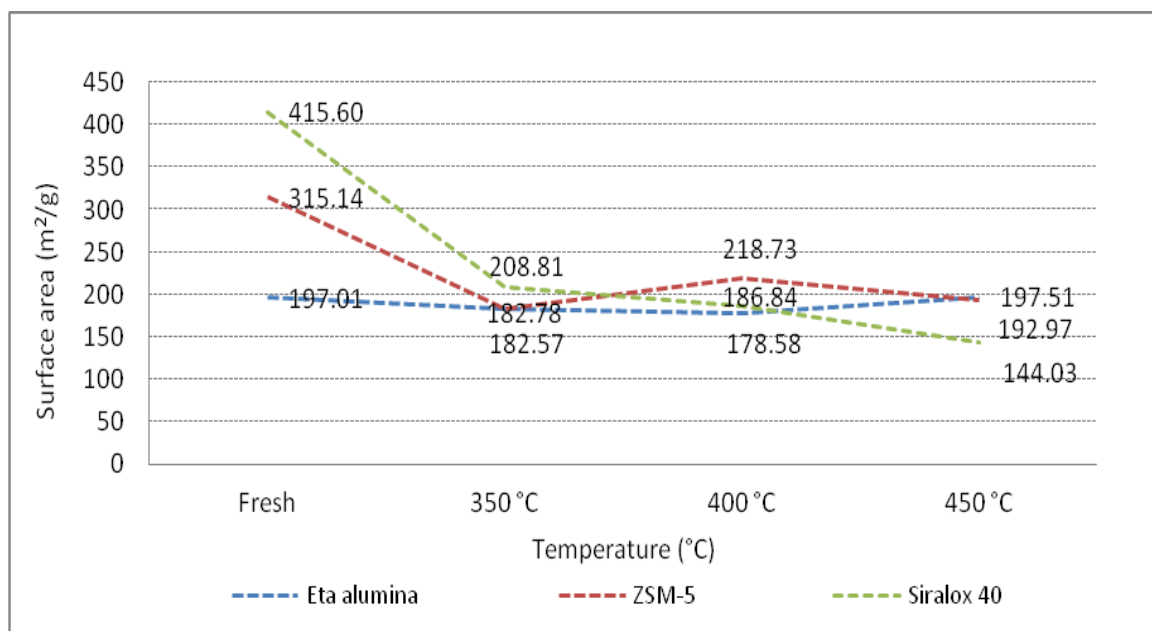
The Eta alumina catalyst was the least coked at 450 °C, and its pore volume and surface area was not affected that much compared to the fresh Eta alumina catalyst. The behaviour of ZSM-5 regarding its carbon content followed the same trend as the other two catalysts. The surface area and pore volume of the ZSM-5 catalyst did not change much from the fresh catalyst to the reactions that took place at 350 °C, 400 °C and 450 °C.



**Figure 7.30: Comparison between carbon content (%) of the three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C**



**Figure 7.31: Comparison between pore volume (cm³/g) of the three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C**



**Figure 7.32: Comparison between surface area (m<sup>2</sup>/g) of the three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C**