
Question 17: What sets the volume gain in ULSD units? How much does lowering the space velocity increase the volume gain? How much volume gain can be expected for each feed component?

Minh Dimas (CITGO)

Volume gain requires hydrogen consumption. Aromatic saturation reactions consume the most hydrogen, followed by olefin saturation. For same feed qualities and same LHSV, the units that make higher cetane product will have higher volume gain due to more aromatic saturation. The main factors for maximum unit volume gain include degree of aromatic saturation, reactor temperature, catalyst type, feed characteristics (aromatic and olefinic content), and space velocity (lower space velocity favors volume gain). However, we do not have data to correlate space velocity and volume gain, specifically.

In general, volume gain for feed components can be listed in decreasing order as follows: Light Cycle Oil, Coker Light Gas Oil, Coker Kerosene, Crude Diesel, Crude Kerosene, and Coker Naphtha. The volume gain to be expected for each feed component is highly dependent on the aromatic and olefinic content (and therefore hydrogen consumption) of those components, so it is difficult to give specific volume gain expectations. It is best to use relative volume gains between specific feed components based on each component's hydrogen consumption and/or aromatic content.

Note that aromatic saturation is reversible at higher reactor temperature. Therefore, for units that process very sour feed, a higher reactor temp will be required to meet the sulfur spec of the diesel product. However, higher temperature may lower the aromatic saturation, and thus, lower the volume gain.

Kaspar Vogt (Albemarle)

Absent from some form of cracking, the volume gain possible is mainly determined by the concentration of aromatics in the feed. At a given set of conditions (feed, pressure and feed rate/space velocity) the aromatic saturation will be determined by the catalyst activity. The desired reactions are the saturation of poly and mono aromatics which are enhanced with NiMo or NiW catalyst at medium and higher pressure vs. CoMo catalyst. Stacked systems of catalyst can optimize the H₂ consumption versus the performance objectives.

Lowering the feed rate will increase the residence time, which is favorable for increased aromatic saturation. However, mono aromatic saturation occurs slowly at typical hydrotreater conditions so density uplift may not be high if polyaromatics are absent from the feed. For individual feed components, the volume gain comes from aromatics saturation and heteroatom removal. The density of paraffins and naphthalene's are not affected significantly in the hydrotreater.

Most ULSD hydrotreaters have a start of run operating temperature in the kinetic regime of the

operating window and will hydrogenate aromatics. Once the unit operates past its maximum saturation temperature, in the thermodynamically controlled regime, net aromatics saturation decreases and volume gain will begin to decrease as well. Continuing to increase the operating temperature will further reduce the volume swell. Operating at the maximum saturation temperature is an operating strategy known as max arosat and maximizes the volume swell as well as Cetane uplift for a ULSD unit.

Shankar Vaidyanathan (Flour)

The volume gain in higher pressure ULSD units handling cracked stocks as a portion of the feed blend is often set by the hydrogen consumption for ring opening and aromatic saturation. A rule-of-thumb is that, approximately 25-30 SCFB chemical hydrogen is consumed for every 1% of aromatics saturation, and the resulting gravity improvement gives 0.1 LV% synthetic volume gain. Assuming HDS objectives are met, the optimum point should be the combination of aromatic saturation, cetane and gravity targets without giving away product specifications in the blended pool. Since hydrogen is neither cheap nor available in unlimited quantity, the catalyst system is often tailored in the ULSD units to minimize hydrogen consumption while just meeting production objectives.

Aromatic saturation is an equilibrium limited reversible reaction for a given unit hydrogen partial pressure and a specific catalyst system. Lowering the space velocity will lower the temperature to promote aromatic saturation. In new designs, aromatic saturation through the catalyst cycle is considered while selecting the catalyst system, setting the pressure and configuring the reactor. Some diesel hydrotreaters have a separate aromatic saturation reactor that operates colder with noble metal catalyst and these designs have incremental cetane boost and volume gain. Lowering space velocity in an operating ULSD unit is impractical since reducing the feed rate negates the volume gain benefit.

Charles Olsen (ART)

There are a number of parameters which influence volume gain in a ULSD unit. Hydrogen partial pressure and LHSV are two key operating conditions which have a large effect on the product volume increase. Catalyst selection also plays an important role since at higher pressures NiMo catalysts have a higher aromatics saturation activity compared to CoMo catalysts.

Figure 1 shows the total volume yield on a fresh feed basis that has been achieved in several commercial diesel hydrotreaters as a function of unit LHSV. Generally speaking, as LHSV decreases the potential volume swell increases. At a LHSV around 1 hr⁻¹ or less, total product volume increases of 6-7% or more are achievable (provided the H₂ pressure is high enough), while at a LHSV greater than about 1.7 hr of the total product volume increase is about 1-2%.

Of course LHSV is not the only parameter which can influence the volume swell. H₂ partial pressure also has a significant effect. Figure 2 summarizes the total product volume yield as a function of unit pressure for the commercial units shown in Figure 1. Not surprisingly, higher pressure units tend to achieve much higher level of volume swell. In these examples, the volume increase is typically less than 3% when the unit pressure is less than 1000 Psig. The total volume swell increases to the 4-7% range as pressure increases beyond 1000 Psig. The data in figures 1 and 2 also suggest there is a practical limit to the volume swell achieved from typical hydrotreating. A Comparison of the volume swell achieved by Refiners A and B shows they are roughly the same for both units despite the large difference in operating pressure at similar LHSV.

The volume swell also varies significantly with feedstock. Figure 3 summarizes how the total product volume yield correlates with the API gravity of the feed. In general, the product volume swell increases as the feed API decreases. In other words, as more FCC LCO is added to the feed the potential volume swell from hydrotreating increases. As mentioned previously, the catalyst will also have an impact on the degree of volume swell achieved in a hydrotreater. It is well known that NiMo catalysts have higher aromatic saturation activity than CoMo catalysts, and therefore a NiMo catalyst is expected to deliver greater volume swell. Figure 4 summarizes pilot plant data which demonstrates this. These data were generated using a 25% LCO containing feed and shows that the NiMo catalyst results in 1-2 numbers higher total product volume increase compared to the CoMo catalyst.

Raj Patel (Haldor Topsoe, Inc.)

In ULSD units, volume gain is achieved through HDS, aromatics saturation, and hydrocracking if converting diesel into naphtha is desirable. The type of feedstock and operating conditions such as pressure and catalyst volume will set the amount of volume swell. Lowering the space velocity will increase the aromatics saturation if the operating temperature is in the kinetic-controlled regime. There is a significant difference in volume swell for different type of compounds, and the volume swell is therefore very dependent on the feedstock. Obviously, the feed that has the most sulfur, olefins and/or aromatics will give you the highest volume swell since it will consume the most hydrogen. If the refiners are trying to maximize volume swell, then they should operate their existing hydrotreating unit at the highest hydrogen partial pressure possible and utilize catalyst that has a high hydrogenation function. Topsoe's NiMo BRIMTM catalyst are specifically designed to utilize the Brim catalyst sites as well as the Type II site for maximizing HDS, HDN and HDA activity resulting in a high-volume swell. For a grassroots design, consideration should be given to a two-stage design with aromatic saturation catalyst in the second stage to maximize volume swell.

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