

Mixing Effects in Dead End Hydrogenation of Oils: Sulfite Oxidation Model

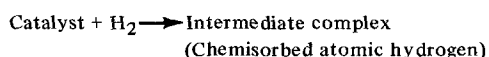
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ABSTRACT

Most industrial hydrogenators are of the dead end type where the gas is bubbled at the bottom of the apparatus, builds up a certain pressure on top of the oil, and is not recirculated. The hydrogen needed by the reaction comes partly from the fraction of the bubbles that is absorbed and partly from the gas space. It was found that sodium sulfite oxidation follows the same mixing pattern, i.e., the highest rate of oxidation always occurred in the upper half of the liquid and correlated strongly with the Reynolds number of the turbine. It is shown that for Reynolds numbers above 600 the optimum impeller position is about two thirds the liquid height measured from the bottom of the vessel. Information is given regarding the variations in selectivity, isomerization and hydrogenation of oils when the speed, relative location and dimensions of the turbine are varied.

INTRODUCTION

Hydrogenation of fatty materials involves not only several consecutive and simultaneous chemical reactions, but also physical steps of mass transfer to and from the catalyst surface. It is recognized that the reaction mechanism probably goes through the following sequence:



Several other reactions take place at the same time. The double bond in fresh naturally occurring triglycerides appears in the *cis*-form, and during hydrogenation the *trans*-isomer is formed. Geometrical isomerization is always accompanied by positional isomerization where the double bonds migrate along the chain. Simultaneously with isomerization appears the phenomenon of selectivity, defined here as the preferential hydrogenation of the polyunsaturated acids relative to monounsaturated groups. Both selectivity and isomerization are affected by the operating variables and, by proper control, it is possible to obtain a wide range of hydrogenated products exhibiting different physical properties.

A large number of papers have been published reporting the effects of pressure, temperature, catalyst concentration and agitation on the rates of hydrogenation, selectivity and isomerization. Their real significance on the chemical reactions involved can be evaluated only when mass transfer resistances are minimized. Mass transfer resistance corresponds here to the resistance encountered by hydrogen when diffusing from the gas space and through the liquid towards the catalyst surface. Only four investigations (1-4) are known in which these resistances were substantially reduced and their conclusions should be important for evaluating the true effect of operating variables.

It is generally accepted that agitation rates play an important role in determining whether or not mass transfer effects are significant. Experimental results have indicated that mixing patterns that provide a low concentration of

hydrogen on the catalyst surface may produce more selective and more isomerizing reactions than those that tend to enrich the surface with hydrogen. Unfortunately, no quantitative criterion is available to describe the degree of turbulence achieved with a certain number of rotations per minute. In most cases the reported experimental data are representative only of the equipment used and not of the reaction itself.

Industrial hydrogenations are usually carried out in a dead end reactor where the gas is bubbled at the bottom of the apparatus, builds up a certain pressure on top of the oil, and is not recirculated. Hydrogen requirements are fulfilled by the fraction of the bubbles that is absorbed and by the dead gas space. Agitation is usually provided by one or more impellers located on a central shaft.

Only three papers have so far reported on the effect of impeller geometry and location upon the rate of reaction. In 1961, Wisniak and Albright (4) indicated qualitatively that the best position for the impeller seemed to be at two thirds of the liquid height, a figure radically different from that used in an opened gas liquid contactor where optimum rates are achieved when the turbine is positioned at one third of the liquid height. Wisniak and Stefanovic (5) investigated the effect of turbine location at different temperatures and rates of mixing and found that for every case there exists a definite relative height which will provide the optimum conditions for gas liquid contact and improvement in the rates of solution and reaction of the hydrogen. Under conditions in which the process was controlled by the chemical reaction (low temperature and low pressure), the effect of the relative height was small, the turbine being located at 50-57% of the liquid height. Conditions that favored the chemical reaction, such as pressure and temperature increases, enhanced the level effect, shifting the maximum reaction rate to higher levels. Thus, at 145 C, with clear control of mass transfer, the turbine needed to be positioned at about 75% of the liquid height measured from the bottom of the vessel. It was explained that, for high chemical resistance, hydrogen bubbling through the liquid was enough for satisfying the reactions needs and the agitator had to be located deep into the liquid in order to provide appropriate dispersion. But when chemical resistance was small, the reaction proceeded very rapidly and the bubbling hydrogen was not enough, thus increasing the importance of the gas on top of the liquid. The agitator had to be put closer to the surface in order to draw in the balance of the gas, as well as to insure its proper dispersion.

Influence of the gas above the solution was studied by Boerma and Lankester (6). In their work, they passed CO₂ on top of a solution of sodium carbonate and studied the absorption velocity as a function of mixing rate and position of the impeller. Their findings indicated that, in general, the optimum impeller position was about 80% to 90% of the liquid height, and that under a certain rotations per minute there was no significant absorption of CO₂. In other words, the head gas and the upper liquid layers were important only above a certain degree of mixing.

The literature survey indicated the advantages of trying to visualize the mass transfer effects in order to give some additional rules for optimization. It was equally important

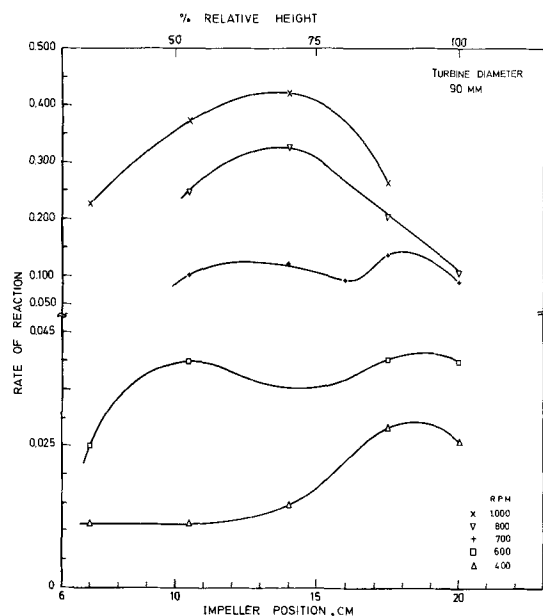


Fig. 1. Variation of rate with impeller position. Sulfite oxidation.

to know how isomerization and selectivity of hydrogenation were affected by these phenomena. For these purposes it was decided to use the sulphite oxidation method as a model for the reaction, using a transparent dead end reactor.

The oxidation of sodium sulphite has been extensively used to study the characteristics of mass transfer with simultaneous chemical reaction. Although its mechanism is still not clearly understood, it is known (7) that at sulfite concentrations higher than 0.08 M the reaction is first order with respect to oxygen and zero order with respect to sulfite. Under 0.02 M it is first order with respect to sulfite and oxygen. The reaction is very sensitive to traces of

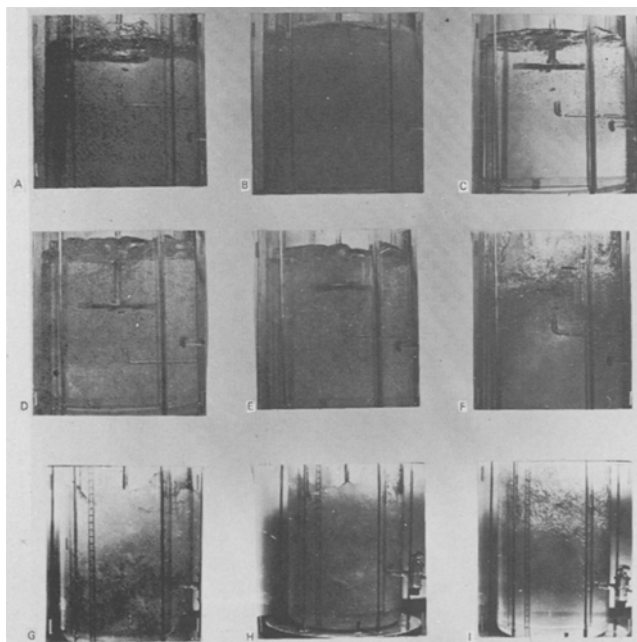


Fig. 2. Mixing patterns. Sulfite oxidation.

	A	B	C	D	E	F	G	H	I
Turbine diameter, mm	60	60	90	90	90	90	150	150	150
Speed, rpm	600	800	400	600	600	600	400	400	400
Relative height, %	95.3	83.3	83.3	66.6	83.3	95.3	50.0	83.3	95.3
Reynolds number	216	288	324	486	486	486	900	900	900

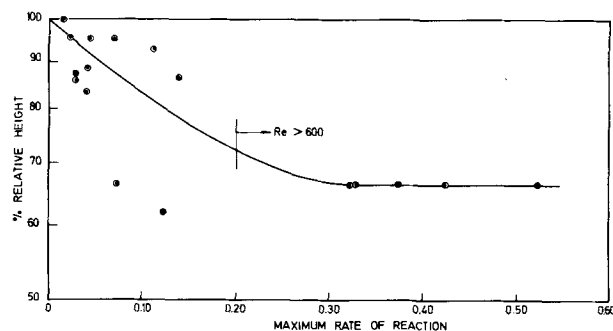


Fig. 3. Maximum rates at different relative heights and Reynolds number (Re , defined as $D^2N/100$, cm^2/min). Sulfite oxidation.

catalyst, but it is generally preferable to work with cobalt ions as catalyst because the latter are more active and less sensitive to impurities.

EQUIPMENT AND EXPERIMENTAL TECHNIQUES

Sulfite oxidation runs were made in a glass vessel 32 x 35 cm, provided with a plastic cover with openings for the agitator shaft, gas sparger, thermometer and manometer. The shaft and the sparger could be raised at will, but in all runs their relative distance was kept constant. Four standard turbines with diameters 60, 90, 120 and 150 mm were used. They were made from brass and covered with an epoxy varnish to avoid possible catalytic effects. Agitation was provided with a Servodyne arrangement that allowed speed variation between 200 and 1000 rpm. The apparatus was filled with distilled water to one vessel diameter high and enough prophoto grade sodium sulfite was added to make a 0.15 N solution. A sample was taken and then cobalt sulfate catalyst added to a total concentration of 10^{-4} M. Oxygen flow was started when the agitator achieved a predetermined speed, and a constant gage pressure of 2 cm Hg was maintained during all runs. Samples were taken and the rate determined from the initial concentration. They were analyzed by iodometry, taking special care in minimizing contact with air. In all of the runs temperature was maintained between 19 and 21 C, and reproducibility of results was within $\pm 10\%$.

Hydrogenation runs were made in a dead end batch autoclave Model Magnedrive, manufactured by Autoclave Engineers, Inc., for a maximum working pressure of 5000 psi at 650 F. The equipment and its operation were similar

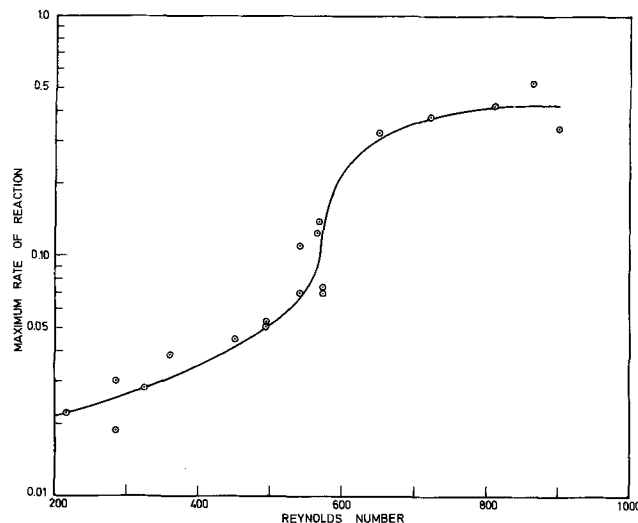


Fig. 4. Influence of Reynolds number (defined as $D^2N/100$, cm^2/min) on maximum rate of reaction. Sulfite oxidation.

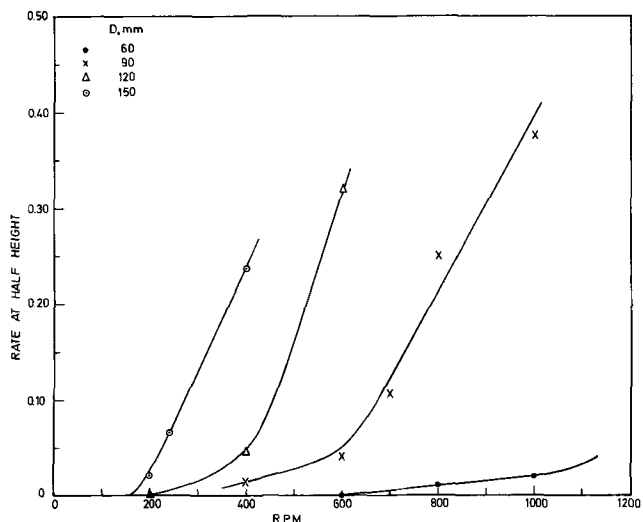


Fig. 5. Effect of impeller speed at constant depth. Sulfite oxidation. D, turbine diameter.

to those reported previously (4,5). Agitation was provided by a Dispersimax turbine with a diameter 40% that of the autoclave and driven by a variable speed motor. Two baffles located 180 degrees apart helped provide turbulence. Heating was provided by an electric mantle connected to an automatic temperature controlling instrument. Cooling and additional heating were provided by an internal coil, and by proper use of the water valve it was possible to control temperature to within ± 2 C. The effect of the turbine location could only be studied by varying the amount of oil being treated.

SULFITE OXIDATION RUNS

A total of 75 runs were made at different mixing rates and turbine relative heights. Figure 1 represents the variation of the rate of reaction for a given impeller diameter. The curves shown are characteristic for all of the runs, passing through a maximum that was always located in the upper half of the liquid. Using a Reynolds number defined as $D^2N/100$ it was possible to distinguish three mixing regimes. For Reynolds numbers under 480, bubble dispersion was incomplete and the bubbles did not appear to fill all of the vessel. At high relative heights (80-95%) a vortex was always generated, but the lower part of the reactor was extremely impoverished in bubbles. These phenomena are illustrated in Figures 2a, 2b and 2c. At intermediate Reynolds numbers (480-600) there was better dispersion of the bubbles in the liquid, particularly when the relative height did not exceed 85%. Higher relative heights originated a vortex with a corresponding decrease in bubble concentration in the lower section (Fig. 2d, 2e and 2f). Baffles were seen to be important in directing the bubble flow downwards (Fig. 2f). When the Reynolds

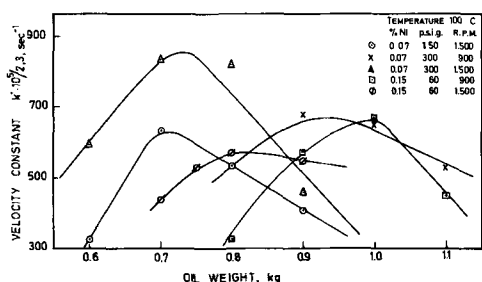


Fig. 6. Effect of relative height on hydrogenation rate. k' velocity constant, sec^{-1} .

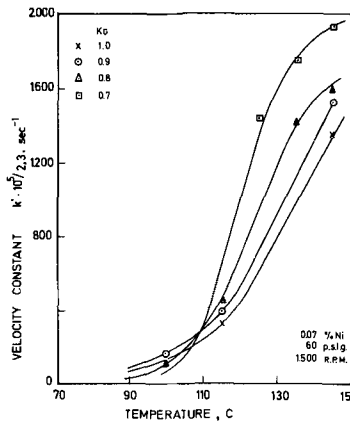


Fig. 7. Effect of temperature. Hydrogenation.

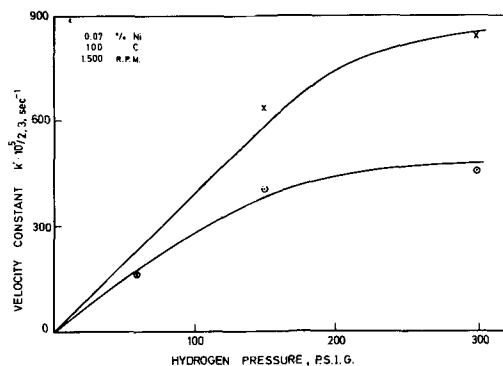


Fig. 8. Effect of pressure. Hydrogenation. \circ , 0.9 kg oil, x oil level at maximum k' .

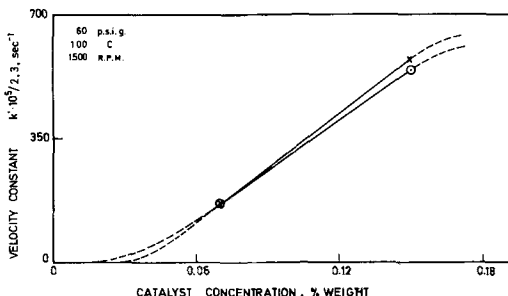


Fig. 9. Effect of catalyst concentration. Hydrogenation. \circ , 0.9 kg oil, x oil level at maximum k' .

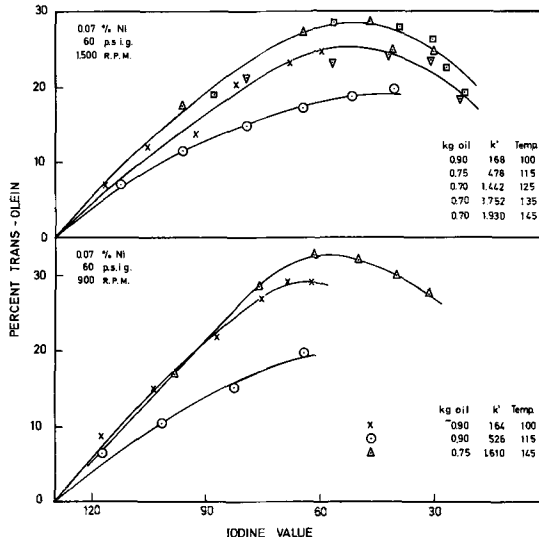


Fig. 10. Isomerization effects during hydrogenation. k' , velocity constant, sec^{-1} .

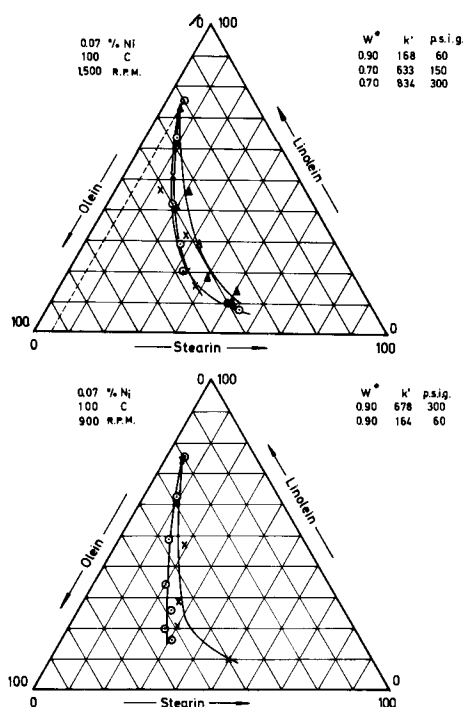


Fig. 11. Selectivity of hydrogenation. k' , velocity constant, sec⁻¹.

number exceeded 600, there was an excellent dispersion through all of the vessel and, in most cases, the maximum rate of reaction was attained when the impeller was at two thirds of the liquid height measured from the bottom of the vessel. At this particular value considerable foaming of the solution took place, so that the real position of the impeller was even lower. An increase in relative height decreased the quality of the dispersion, as shown in Figures 2g, 2h and 2i.

The oxidation of sodium sulfite is a very rapid reaction, so that the rate of oxidation is determined by mass transfer effects, that is to say, on the possibility of contact between oxygen and the solution. For this reason there are two problems that develop inside the vessel: the need for a good and efficient mixing of the liquid, and the need for a good contact between the head gas and the solution itself. The agitator disperses the bubbles that emerge from the sparger and breaks up the surface of the liquid. The relative intensity of these two phenomena will undoubtedly depend on the position of the mixing device. When the agitator is at 33% to 67% of the liquid height there is good mixing but poor contact at the surface. Increasing the relative height will slowly generate a vortex that will pump additional gas into the solution, foaming the surface and increasing the interphase. From this it can be inferred that for every set of conditions a compromise will exist between good mixing and surface breaking that will maximize the rate of reaction. When the agitator is operated at low speeds, the mixing is very inefficient at all heights and there seems to be little advantage in bubbling gas through the liquid since a larger interphase area can be created by vortex action. In other words, it can be expected that better reaction rates will be achieved with the impeller located high in the liquid, e.g., 85-95%. On the other hand, high speeds or Reynolds numbers will improve the mass transfer and, consequently, accelerate the reaction. Therefore, a higher flow through the sparger will be needed to maintain the rate. This will require lowering the impeller in order to be able to produce a proper dispersion of the bubbles. A certain critical position will have to be reached where an additional decrease in relative height will offset the better dispersion with a decrease in the head gas drawn in. Increasing the relative height will produce exactly the opposite phenome-

non; gas drawing will increase, but bubble dispersion will diminish. From Figures 3 and 4 it appears that above a Reynolds number of 600, the compromise height is very critical and remains constant at about two thirds of the liquid height.

The intermediate range of Reynolds numbers seems to be unstable, as shown by Figure 3. It is quite possible that in this range there is either an undefined zone, or two ways to pass from low to high Reynolds number. This is corroborated by Figure 1 where it is seen that two maxima appear. This fact was not found at lower Reynolds number, although it is possible that it was hidden by the experimental error.

The combination of these factors will determine an impeller position that will best satisfy the requirements. It is then postulated that the turbine will occupy a position in the liquid such that the distance from the bottom of the reactor be the maximum compatible with a complete and uniform dispersion of the reacting gas, and that the distance to the liquid level be such that by taking advantage of the two ways of dissolving the oxygen, sufficient quantity of the gas will be available.

The influence of impeller speed at constant depth (50%) and variable diameter is shown in Figure 5. It is seen that below a certain speed, agitation does not seem to have much influence on the reaction rate. This fact has already been mentioned (6,8), although with a different set up. Below this particular speed there is no improvement in the reaction rate caused by the mixing. The impeller does not seem to be able to break the bubbles in a manner sufficient to create additional area. The reaction is caused by direct contact of the emerging bubbles and surface agitation. It is very probably that both phenomena are of the same order.

HYDROGENATION RUNS

A total of 116 runs were made with sunflower oil, in the following range of variables: temperature, 100 to 145 C; pressure, 60 to 300 psi; catalyst concentration, 0.07% to 0.15% Ni by weight; agitation, 600 to 1800 rpm; oil weight, 0.50 to 2.0 kg. In all of the runs it was found that after an initial induction period the data could be correlated by a pseudo-first order reaction. For this reason all of the kinetic data were expressed as the overall reaction rate constant, k' sec⁻¹.

Effect of Turbine Location

Figure 6 indicates some typical results under various process conditions. It is seen that in every case the rate goes through a maximum that depends on the relative intensity of mass transfer and chemical effects. The position of the impeller is directly related to the weight of the oil being hydrogenated, smaller weights corresponding to the impeller's being located closer to the liquid surface.

Figure 6 constitutes another proof of the fact that reaction rates in dead end reactors can be drastically increased by a simple change in the position of the impeller.

Temperature

In Figure 7 appear the values of k' at 1500 rpm for different reactions temperatures. It can be seen that the data follow a typical sigmoid curve, and that the rate of reaction duplicates itself for temperature differences between 3 and 17 C, according to the oil level being used. Similar results were obtained at 900 rpm.

Pressure

The effect of hydrogen pressure is shown in Figure 8. Similar to the results of Wisniak and Albright (4), it was found that the relation was exponential, with an exponent smaller than unity. The effect of the liquid level can be inferred from the same Figure. For the indicated operating

conditions and the oil level which corresponds to the maximum of the 1500 rpm curve, the value of the velocity constant k' increased 64% at 150 psig and 71% at 300 psig, with respect to the value attained when the level was 0.9 kg.

Catalyst Concentration

In Figure 9 are plotted the values of the velocity constant k' and catalyst concentrations for liquid levels of 0.8 and 0.9 kg and 1500 rpm. It can be seen that the variable has little effect within the range of operating conditions. Actually, the maximum value of k' changes by no more than 15% when the oil level varied between 0.7 and 1.1 kg.

Isomerization

In general it was found that the curve per cent-*trans* isomers vs. iodine value increased from zero to a maximum value located in the range 60-40 of iodine value, then decreasing as the hydrogenation proceeded. The diene content decreased when the pressure and the agitation were increased, larger quantities of *trans* isomers being formed at higher temperatures. No general tendency could be detected for the effect of catalyst concentration changes. Nevertheless, it is not possible to make a strict separation of operating variables. Thus, as shown by Figure 10, although increasing the rate of agitation from 900 to 1500 rpm decreases the formation of *trans* isomers, the *trans* content is minimum for 115 C, and intermediate value in the temperature range considered.

With respect to the oil level, it was found that larger amounts of *trans* isomer were present in the maximum of the curves that relate the oil level to the rate constant k' .

Selectivity

Since the purpose of the present work was to establish general trends, it was considered sufficient approximation to take only the C_{18} acids for plotting ternary diagrams for the study of selectivity. In general, it was found that selectivity varied in a fashion similar to isomerization. Thus, more selective hydrogenations were obtained at lower agitation rates and higher temperature and catalyst concentration levels. As shown by Figure 11, as increase in pressure produced a less selective reaction.

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