

TECHNOLOGY

SYNERGISTIC EFFECTS IN OXIDATION OF PARAFFINS TO SYNTHETIC FATTY ACIDS

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In [1] we examined physical phenomena accompanying the compounding of paraffins that are used as raw material for the production of synthetic fatty acids (SFA). In the present article we will present certain experimental data on the oxidation of paraffins under laboratory conditions and in a commercial unit at the Volgograd Petroleum Refinery. The production of SFA by the oxidation of paraffins has been investigated quite thoroughly [2, 3], but some of the effects that we observed had not been described previously, and may be of definite interest.

The laboratory unit consists of a 100-cm³ sparged glass reactor equipped with a heating jacket and connections for introduction of the preheated charge and air and the withdrawal of samples. The experiments were performed with components of the feedstock used in the refinery, with a commercial manganese catalyst. The oxidized product was analyzed by standard methods.

It is known that n-paraffins are very resistant to forming free radicals that are capable of "carrying" a reaction chain. In fact, we found that even in the catalytic oxidation of a solid paraffin (melting point 60°C) at 110°C, the induction period was more than 45 h. Under the same conditions, a liquid paraffin (mp 27°C) was not oxidized over the course of about 10 h. As can be seen from Fig. 1, synergistic effects are observed for all mixtures of liquid and solid paraffins, but the greatest deviation from additivity is manifested by mixtures containing 20% or 80% solid paraffin by weight. Also characteristic for these same mixtures [1] is a maximum depression of the crystallization temperature and solidification point. Thus, the structural changes that were noted previously do have a significant influence on the chemical properties of the starting material.

Under commercial conditions, in order to shorten the induction period for the oxidation, it is common practice to return to the feed a paraffin recycle containing a great variety of oxygenates (aldehydes, ketones, alcohols, lactones, etc.), or to blend the fresh paraffin with the unsaponifiables obtained when the fatty acids are separated from the product of the preceding oxidation cycle. According to current views, the above-named oxygenates also enter into the composition of the first and second fractions of the unsaponifiables. At 120-125°C, a commercial mixture containing up to 2/3 of these products can be oxidized with essentially no induction period.

The unsaponifiables themselves, if no fresh paraffin is present, are oxidized to acids at a moderate rate. As can be seen from Fig. 2, a commercial mixture of 33% fresh paraffin and 67% recycled paraffin by weight is oxidized at the highest rate during the initial period. The initial oxidation rates of each of its components are lower; i.e., here also we see a nonadditive influence of each component on the other. Characteristic for the synergistic mixtures is the existence of a certain relaxation time, after which the maximum oxidation effect is manifested. Actually, stepwise or one-time addition of a hot mixture of fresh paraffins to the reactor, where the oxidation of the unsaponifiables has proceeded over the course of 1 h, leads to termination of the process in 1-1.5 h and subsequent reestablishment of the process at a high rate (see Fig. 2).

In view of the mechanism of paraffin oxidation, it is evident that the initial rate of the process can be increased by the use of peroxide compounds as initiators. However, this approach is not used in the commercial process. Also, such a simple method of activating the oxidation as the introduction of the oxidized product has not been used extensively in industry. This reflects the fact that the effect from accelerating the formation of acids in the initial stage usually becomes gradually weaker, and the overall gain in terms of oxidation time does not compensate for losses incurred by introducing the initiator (Fig. 3).

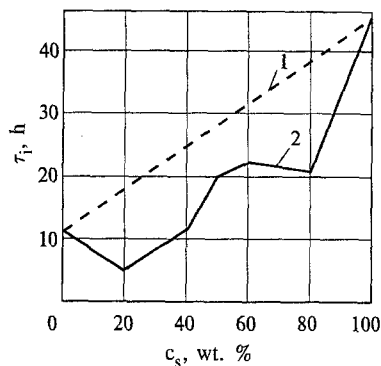


Fig. 1. Oxidation induction period τ_1 as a function of solid paraffin concentration c_s in mixture with liquid paraffin: 1) hypothetical relationship; 2) actual relationship.

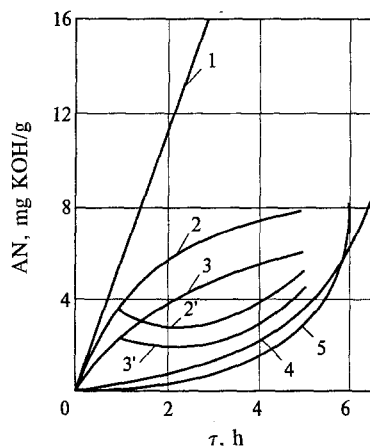


Fig. 2. Acid number (AN) as a function of oxidation time τ for different types of raw material during initial period, at 110°C : 1) commercial mixture (after $\tau_1 = 2$ h); 2,2') first unsaponifiables, before and after addition of fresh paraffin, respectively; 3,3') same, second unsaponifiables; 4) mixture of 80% solid and 20% liquid paraffins ($\tau_1 = 24$ h); 5) mixture of 20% solid and 80% liquid paraffins ($\tau_1 = 5$ h).

Experiments in which the order of introducing the mixture components was changed have shown that when the oxidized product is added, the nature of the relaxation processes does not change; i.e., manifestation of synergistic effects is possible in the oxidation charge. Oxidized products with different acid numbers ($\text{AN} = 27, 40,$ and 74 mg KOH/g) were added to the initial mixture. Blends having an identical initial acid number but containing oxidized product with different degrees of oxidation as the additive are characterized by practically identical initial rates of acid accumulation.

However, the relationship between the oxidation rate (the acid number of the oxidized product) and the concentration of additive ($\text{AN} = 74$ mg KOH/g) is nonlinear (Fig. 4); this is quite inconsistent with the generally accepted kinetic model. It is considered that after the induction period, the mean oxidation rate stays at a maximum for a rather long time. Consequently, the dependence of the acid number on the concentration of oxidized product should be very nearly linear. The position of the extrema, i.e., the optimal concentration of oxidized product, depends on the oxidation temperature. At 110°C , the maximum increase of the initial acid accumulation rate corresponds to a concentration of 2-3% oxidized product, and at 120°C to 5% by weight.

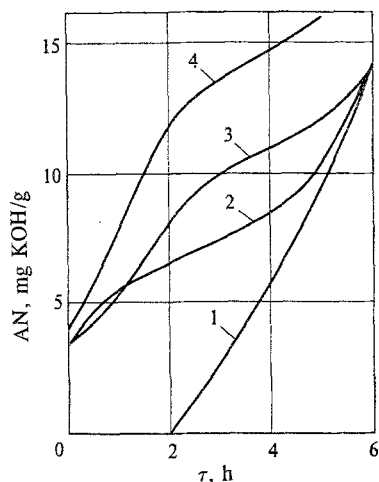


Fig. 3. Acid number (AN) as a function of oxidation time τ during initial period: 1) commercial mixture; 2) first and second unsaponifiables in the presence of 10% oxidized product, with the introduction of a mixture of fresh paraffins after 1.5 h; 3) same, but with the addition of the oxidized product in equal quantities to the unsaponifiables and the fresh paraffin; 4) commercial mixture with 10% oxidized product.

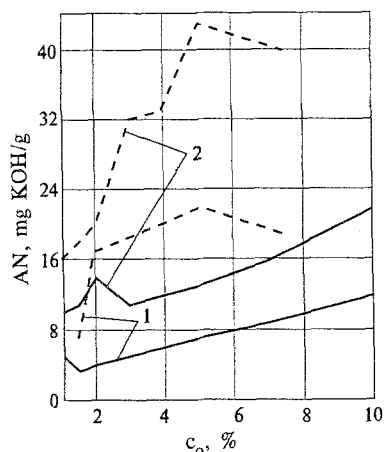


Fig. 4. Acid number (AN) as a function of oxidized product concentration c_o in initial charge, 2 h after the start of oxidation (curves 1) and 4 h after start of oxidation (curves 2). Continuous curves are for oxidation at 110°C, broken curves at 120°C.

The laboratory results were confirmed in the course of experimental-commercial tests in five oxidation columns operating in parallel. Oxidized product in amounts of approximately 5% by weight was added to each of three of the columns; the other two operated in the normal mode (Fig. 5). In all of the columns to which the oxidized product was added, the total oxidation time was reduced by 2-4 h. At 115-120°C, the commercial feed mixture consisting of 2/3 unsaponifiables and 1/3 fresh paraffin begins the oxidation process with hardly any induction period.

It can be seen from Table 1 that the oxidation-containing compounds of various types increase the melting point depression of the paraffin mixture with the composition that is most suitable for oxidation. The alcohol gives the greatest depression. Increases in the concentrations of the oxygenates result in greater effects. It should be noted that when these compounds are present at concentrations greater than 5% by weight, they change the basic character of crystallization of the mixture. Upon solidification in a thin layer, a uniform film is formed, gradually losing its mobility.

TABLE 1

Paraffin mixture*	Concentration of additive, wt. %	Temperature, °C		
		initial melting	melting	initial crystallization
Without additive	0	21,0	41,0	32
With additive palmitic acid (C ₁₆)	2	20,3	39,1	32
	4	20,2	38,0	32
	6	20,0	36,0	No crystals formed
capric acid (C ₉)†	6	20,1	36,1	Same
nonyl alcohol	6	20,2	33,1	"
nonane-5†	6	20,1	36,9	"
caproic aldehyde (C ₆)	6	20,0	36,2	"

*Mixture of 80% liquid and 20% solid paraffins.

†As in Russian original – Translator.

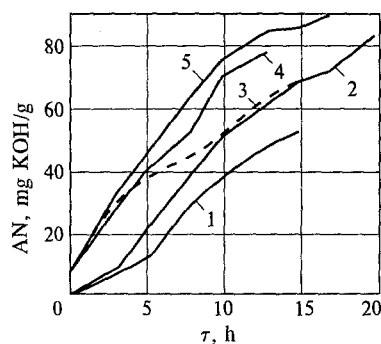


Fig. 5. Acid number (AN) as a function of oxidation time τ in columns of commercial unit: 1, 2) K-9 and K-13 (respectively), without addition of oxidized product; 3, 4, 5) K-16, K-1, and K-14 (respectively), with addition of oxidized product.

The oxidized product also gives a depressant effect. When it is added to the mixture of fresh paraffins, the melting point and crystallization temperature are lowered by 5-6°. The lighter oxidized product, at concentrations less than 10% by weight, also changes the morphology of the crystallized structure.

Fresh paraffin, when it is added to an oxidation charge containing unsaponifiables and oxidized product, retards the oxidation process. However, this effect is less pronounced. If the paraffin was previously blended with the oxidized product and heated for 1 h at the oxidation temperature, and then introduced into the reaction zone, the relaxation time is reduced, and the retardation is less severe. This behavior is quite natural, since in this case the components that are blended are closer in composition and evidently closer in structure.

The data presented in this article demonstrate that, in order to intensify oxidation, particular attention must be given to the preparation of the charge and (no less important) to the ratio of charge components. Further detailed and careful studies will be necessary to achieve this end.

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