Investigations of the Chemical Structure of Sulfonated Amine–Formaldehyde Resins. 4. Variations in Structure with Preparation Procedure

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ABSTRACT: The effect of variations in the preparation procedure on the chemical structure of sulfonated urea–formaldehyde resins was investigated by using ^{13}C NMR. Two variations were considered. The first involved switching the order of the sulfonation and condensation steps, whereas the second variation involved combining the addition and sulfonation steps in one step. The chemical structures of resins prepared according to ASC (addition–sulfonation–condensation) and ACS (addition–condensation–sulfonation) protocols were compared, and it was shown that the ACS protocol leads to resins with a higher molecular weight, whereas the ASC protocol results in resins with a higher degree of sulfonation. Two-step and three-step ASC protocols were also compared. It was found that combining the addition and sulfonation steps in one step resulted in a resin that was very similar to that obtained from a three-step ASC protocol. Therefore, it was concluded that the urea–formaldehyde reaction is much faster than the formaldehyde–sulfite reaction. The bearing that this work might have on product development of sulfonated urea–formaldehyde resins was also discussed.

Introduction

Recent work in our laboratory has demonstrated that sulfonated urea–formaldehyde (SUF) resins can be effectively characterized by ^{13}C NMR.[1,2] The signals of the main structural units of the SUF resin were first identified,[1] and then the individual steps of the resin preparation procedure were investigated.[2] Furthermore, some of the major variables affecting the chemical structure of the SUF resin (namely, the reactant ratios) were studied and analyzed. In that work, the procedure followed in preparing these resins consisted of three steps. The first step was the hydroxymethylation (or addition) step in which formaldehyde and urea were reacted to form mono-, di-, or trimethylolureas. The second step involved sulfonating the product of the first step whereas the third step involved the condensation of the product of the second step. This preparation procedure will be referred to as the ASC protocol where A stands for addition, S for sulfonation, and C for condensation.

This paper examines the effect of variations in the resin preparation protocol on the chemical structure of the SUF resins. ASC and ACS protocols will be compared, and the effect of switching the order of the sulfonation and the condensation steps will be analyzed. Moreover, the effect of combining the addition and sulfonation steps in one step will also be studied, and the two-step (A + SC) and the three-step ASC protocols will be compared.

Experimental Section

Synthesis of the Samples. Resins were prepared in three different protocols: ACS, ASC, and A + SC. The ASC preparation procedure was described earlier[2] and will not be repeated here. Following is a description of the other preparation protocols.

ACS Protocol. A sulfonated urea–formaldehyde resin with a formaldehyde to urea ratio (F/U) of 3.0 and a sulfite to urea ratio (S/U) of 1.0 was prepared according to the following procedure. A total of 262 g of a 24% formalin solution was heated to 80 °C, and the pH of the solution was adjusted to 10.0; 40 g of urea and 198 g of water were added. After 20 min, the pH was lowered to 3.0 and the mixture was heated for 120 min. The pH was then raised to 10.0, and 313 g of a 20% sodium metabisulfite solution was added. After 60 min, the solution was cooled to room temperature and its pH was adjusted to 9.0. The same procedure was followed in preparing SUF resins of different F/U and S/U ratios.

A+SC Protocol. A total of 131 g of a 24% formalin solution was heated for 15 min at 60 °C; 225 g of water were added, the temperature was raised to 80 °C, and the pH was adjusted to 10.0. Then 20 g of urea and 31.67 g of sodium metabisulfite were added. The solution was heated at 80 °C for 60 min. The pH of the solution was then brought down to 3.0 by the addition of 14 N H_2SO_4. The reaction mixture was kept at 80 °C for 60 min. Finally, the pH was raised to 9.0.

NMR Measurement. The experimental conditions and procedure of the NMR measurement were kept exactly the same as in the previous study. Details can be found elsewhere.[2]

Results and Discussion

Sulfonated amine–formaldehyde resins have been traditionally prepared in an ASC type protocol.[3,4] The chemical structure of sulfonated urea–formaldehyde resins prepared in such a protocol was discussed in a previous publication.[2] It was shown that during the sulfonation step methylol groups were substituted by CH_2SO_3H groups, whereas during the condensation step the remaining methylol groups along with -NH and -NH_2 groups were involved in producing oligomers with an average degree of condensation (n) of about 1.5. Switching the order of the sulfonation and the condensation step is expected to increase n and possibly produce an SUF resin with a different chemical structure. Our discussion will start with presentation of the chemical structures of SUF resins prepared according to the ACS protocol and then their comparison with those produced by the ASC protocol. Furthermore, the effect of combining the addition and sulfonation steps in one step will also be studied and analyzed.

ACS Protocol. SUF resin with a F/U ratio of 3.0 and S/U ratios of 0, 0.5, and 1.0 were prepared, and the chemical structure of the reaction mixture was studied after each of the reaction's three steps.

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Table I
Concentration of the Functional Groups after the First Step (F/U = 3.0)

δ, ppm	assignt	S/U = 0	S/U = 0.5	S/U = 1.0	ACS av	ASC av
162.0	NH_2CONH-	0.11	0.16	0.14	0.14	0.14
160.2	$-NHCONH-$	0.44	0.39	0.46	0.43	0.43
159.8	$-NHCON<$	0.16	0.04	0.16	0.12	0.12
156.3–154.4	–CO– cyclic	0.29	0.41	0.24	0.31	0.30
82.5	$HOCH_2OH$	0.31	0.33	0.35	0.33	0.34
78.5–78.0	$-CH_2OCH_2-$ cyclic	0.72	0.65	0.75	0.71	0.65
75.0	$>NCH_2O-$	0.08	0.14	0.07	0.10	0.08
71.2	$>NCH_2OH$	0.17	0.19	0.20	0.19	0.26
69.0	$-NHCH_2O-$	0.16	0.14	0.10	0.13	0.17
68.3–68.0	$>NCH_2OH$ cyclic	0.63	0.60	0.62	0.62	0.57
64.7	$-HNCH_2OH$	0.92	0.93	0.91	0.92	0.90

Table II
Concentration of Functional Groups after the Condensation Step (F/U = 3.0)

δ, ppm	assignt	S/U = 0	S/U = 0.5	S/U = 1.0	average	addition step
162.0	NH_2CONH-	—	—	—	—	0.14
160.2	$-NHCONH-$	0.43	0.46	0.42	0.44	0.43
159.8	$-NHCON<$	0.26	0.31	0.30	0.29	0.12
156.3–154.4	–CO– cyclic	0.31	0.23	0.28	0.27	0.31
86.7	$-OCH_2OH$	0.08	0.08	0.08	0.08	
82.5	$HOCH_2OH$	0.71	0.62	0.67	0.67	0.34
78.5–78.0	$-CH_2OCH_2-$ cyclic	0.84	0.81	0.88	0.84	0.69
75.0	$>NCH_2O-$	0.03	0.02	0.03	0.03	0.09
71.2	$>NCH_2OH$	0.20	0.18	0.20	0.19	0.22
69.0	$-NHCH_2O-$	—	—	—	—	0.15
68.3–68.0	$>NCH_2OH$ cyclic	0.42	0.44	0.44	0.43	0.61
64.7	$-HNCH_2OH$	0.23	0.29	0.32	0.28	0.92
53.5	$>NCH_2NH-$	0.14	0.24	0.14	0.17	—
50.3	$>NCH_2N<$ cyclic	0.21	0.21	0.13	0.18	—
47.0	$-NHCH_2NH-$	0.11	0.10	0.12	0.11	—

Table III
Concentration of the Functional Groups after the Sulfonation Step (F/U = 3.0)

δ, ppm	assignt	S/U = 0	S/U = 0.5	S/U = 1.0	condensn step
160.2	$-NH\underline{C}ONH-$	0.42	0.32	0.26	0.44
159.8	$-NH\underline{C}ON<$	0.27	0.46	0.47	0.29
159.5	$-NH\underline{C}ONHCH_2SO_3^-$	—			—
159.0	$-NH\underline{C}ON\langle^{\nearrow}_{\searrow CH_2SO_3^-}$	—	0.06	0.16	—
156.3–155.4	–$\underline{C}$O– cyclic	0.31	0.16	0.11	0.27
86.7	$-O\underline{C}H_2OH$	0.05	0.04		0.08
82.5	$HO\underline{C}H_2OH$	0.65	0.69	0.60	0.67
78.5–78.0	$-\underline{C}H_2OCH_2-$ cyclic	0.75	0.46	0.26	0.84
75.0	$>N\underline{C}H_2O-$	0.03	0.22	0.53	0.03
71.2	$>N\underline{C}H_2OH$	0.23	0.26	0.19	0.19
68.3–68.0	$>N\underline{C}H_2OH$ cyclic	0.38	0.25	0.05	0.43
64.1	$-NH\underline{C}H_2OH$	0.37	0.24	0.17	0.28
62.5	$>N\underline{C}H_2SO_3^-$	—	0.11	0.04	—
60.4	$>N\underline{C}H_2SO_3$ cyclic	—			
57.0	$-NH\underline{C}H_2SO_3^-$	—	0.35	0.66	—
53.5	$>NCH_2NH-$	0.19	0.15	0.21	0.17
50.3	$>NCH_2N<$ cyclic	0.20	0.11	0.12	0.18
47.0	$-NHCH_2NH-$	0.11	0.13	0.17	0.11

The addition (hydroxymethylation) step was conducted under basic conditions, and Table I presents the results of the ^{13}C NMR determination of the functional groups of the reaction mixture. The three experiments shown are for S/U of 0, 0.5, and 1.0, respectively. But since these samples are taken after the first step, the concentration of the functional groups is expected to be the same. A close examination of the contents of the first three columns of Table I shows that if one accepts an average of 13% scatter in data (due to errors in resin preparation and NMR calculations), then it can be concluded that the reaction mixtures resulting from these experiments are comparable. The remaining two columns in Table I compare the concentration of the functional groups of this study and a previous one where SUF resins were prepared in an ASC protocol.[2] Since the first step is the same in both protocols, the concentration of the functional groups should be the same. Table I shows that this is indeed the case.

The concentration of the functional groups after the condensation step is shown in Table II. Before the change in the concentration of these functional groups is discussed, it should be mentioned that for the three experiments (S/U = 0, 0.5, and 1.0) the concentrations of these species should be the same since sulfonation is carried out only at a later stage. To within 10% error, Table II shows that the concentration of the functional groups is comparable.

To facilitate the task of examining the changes in the concentration of functional groups, two additional columns are included in Table II. The first contains the average concentration of the functional groups after the condensation step, whereas the second column presents the concentration of a given functional group after the end of the addition step.

In going from the first to the second steps data, one finds that the concentration of the methylol groups is drastically reduced. A total of 70% of methylol groups bonded to a secondary nitrogen (eq 1) disappeared, whereas

$$-NH-CH_2OH + H_2N- \xrightarrow[-H_2O]{} -NH-CH_2-NH- \tag{1a}$$

$$-NH-CH_2OH + HN< \xrightarrow[-H_2O]{} -NH-CH_2-N< \tag{1b}$$

$$>N-CH_2OH + H_2N- \xrightarrow[-H_2O]{} >N-CH_2-NH- \tag{2a}$$

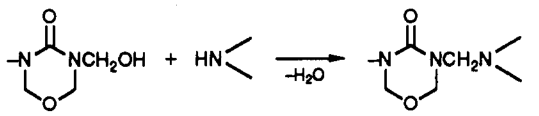
$$>N-CH_2OH + HN< \xrightarrow[H_2O]{} >N-CH_2-N< \tag{2b}$$

only 14% of methylol groups bonded to a tertiary nitrogen (eq 2) disappeared, thus leading to the conclusion that methylol groups bonded to secondary nitrogen are more reactive. Note that only reactions leading to the formation of methylene bridges have been considered. Dimethylene ether bridges were not detected. They are believed to be unstable in acidic media and are probably destroyed forming methylene bridges (eq 3).

$$>N-CH_2OCH_2-N< \xrightarrow{H^+} >N-CH_2-N< + CH_2O \tag{3}$$

This is supported by the fact that the concentration of methylene glycol increases and small amounts of hemiformals are formed. Going back to eqs 1 and 2, one expects the appearance of signals due to the methylene bridges. Table II shows that this is the case. Also, as expected, the concentration of the $H_2NCONH-$ decreases (actually it goes to zero) whereas the concentration of the $-NHCON<$ increases.

By examining the signals due to the cyclic structures, one finds that dimethyloluron is fairly stable under the low-pH condensation conditions (156.3–155.4 ppm signal is unchanged). However, the concentration of the cyclic $-CH_2OH$ decreases (from 0.61 to 0.43 M) and a new signal at 50.3 ppm appears (its concentration is 0.18 M, which is 0.61 M − 0.43 M). It is postulated that urons condense to give



(4)

With this information the degree of condensation (n) can now be calculated from

$$n = \frac{1}{1-[CH_2]} \qquad [CH_2] = \text{relative concentration of methylene bridges}$$

$$= \frac{1}{1-(0.11+0.17+0.18)} = 1.85$$

It must be added that the structure is relatively linear and no signal for $>N-CH_2-N<$ (eq 2b) could be detected.

Table IV
Concentration of Functional Groups in SUF Resins after a Three-Step Preparation Procedure

assignt	S/U = 0.5 ASC	S/U = 0.5 ACS	S/U = 1.0 ASC	S/U = 1.0 ACS
$NH_2\underline{C}ONH-$	—	—	—	—
$NH_2\underline{C}ONHCH_2SO_3^-$	—	—	—	—
$-NH\underline{C}ONH$	0.30	0.32	0.13	0.26
$-NH\underline{C}ON<$ $-NH\underline{C}ONHCH_2SO_3^-$	0.51	0.46	0.56	0.47
$-NH\underline{C}ON{<}_{CH_2SO_3^-}$	0.12	0.06	0.28	0.16
$-\underline{C}O-$ cyclic	0.07	0.16	0.03	0.11
$-O\underline{C}H_2OH$	0.08	0.04	0.04	
$HO\underline{C}H_2OH$	0.64	0.69	0.54	0.60
$-\underline{C}H_2OCH_2-$ cyclic	0.58	0.46	0.31	0.26
$>N\underline{C}H_2O-$	0.05	0.22	0.02	0.53
$>N\underline{C}H_2OH$	0.26	0.26	0.22	0.19
$-NH\underline{C}H_2O-$	—	—	—	—
$> N\underline{C}H_2OH$ cyclic	0.34	0.25	0.13	0.05
$-NH\underline{C}H_2OH$	0.37	0.24	0.24	0.17
$> N\underline{C}H_2SO_3^-$	small	0.11	0.11	0.04
$> N\underline{C}H_2SO_3^-$ cyclic	small	—	0.10	—
$-NH\underline{C}H_2SO_3^-$	0.51	0.35	0.88	0.66
$>N\underline{C}H_2NH-$	0.10	0.15	0.16	0.21
$>N\underline{C}H_2N<$ cyclic	0.05	0.11	0.07	0.12
$-NH\underline{C}H_2NH-$	0.12	0.13	0.13	0.17
$n = 1/(1-[CH_2])$	1.4	1.6	1.5	2.0

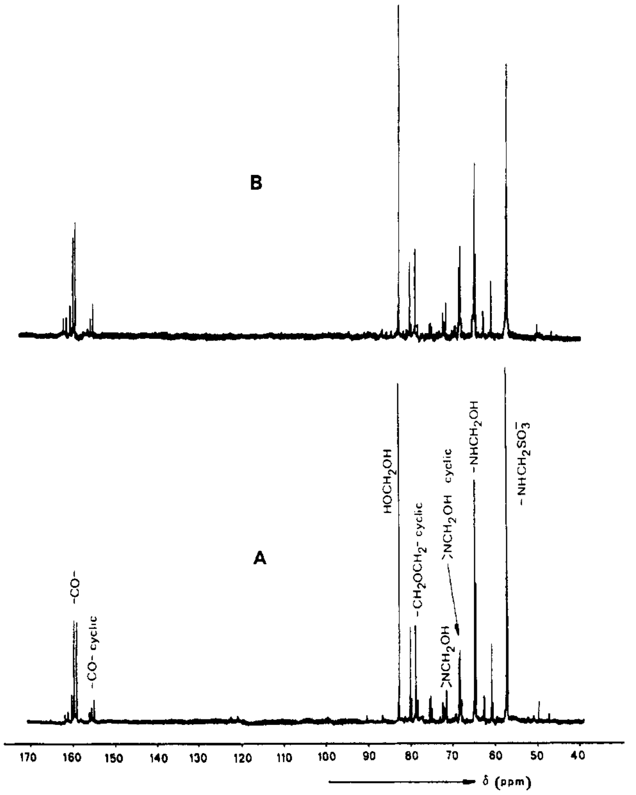


Figure 1. ^{13}C NMR spectra of SUF resins, F/U = 3; S/U = 1, prepared in an ASC protocol. (A) After separate A and S. (B) After combined A + S.

Variations in the chemical structure between resins of the three experiments are expected to show after the sulfonation step. The importance of the experiment where no sulfonation (S/U = 0) takes place is in establishing that whatever changes take place during this step are due to sulfonation and not anything else (such as additional condensation). Table III shows the concentration of the functional groups after the sulfonation step. With comparison of the concentration of these groups for the S/U

Table V
Comparison of the Concentration of Functional Groups Obtained from Two- and Three-Step ASC Protocols

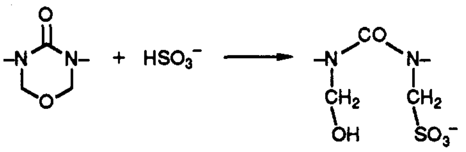
	F/U = 3.0, S/U = 0.5		F/U = 3.0, S/U = 1.0		F/U = 2.0, S/U = 0.5		F/U = 2.0, S/U = 1.0	
	ASC	A + SC	ASC	A + SC	ASC	A + SC	ASC	A + SC
$HOCH_2OH$	0.64	0.60	0.54	0.57	0.25	0.22	0.16	0.22
$-CH_2OCH_2-$ cyclic	0.58	0.51	0.31	0.30	0.18	0.18	0.06	0.05
$>NCH_2OH$	0.26	0.22	0.22	0.17	0.13	0.11	0.10	0.08
$-CH_2OH$ cyclic	0.34	0.24	0.13	0.15	0.04	0.06	0.03	small
$-NHCH_2OH$	0.37	0.26	0.24	0.22	0.23	0.21	0.20	0.18
$-NHCH_2SO_3^-$	0.51	0.41	0.88	0.86	0.51	0.48	0.98	0.92
degree of sulfonation, %	100	100	100	100	100	100	100	100
$n = 1/(1 - [CH_2])$	1.3	1.6	1.4	1.3	2.2	2.5	1.5	1.5

= 0 and the condensation step columns, it is readily verifiable that no significant changes occur during this step when no bisulfite is added to the reaction mixture.[2] The other two columns of Table III show the considerable changes in the concentration of functional groups that occurred after sulfonation (S/U = 0.5 and 1.0).

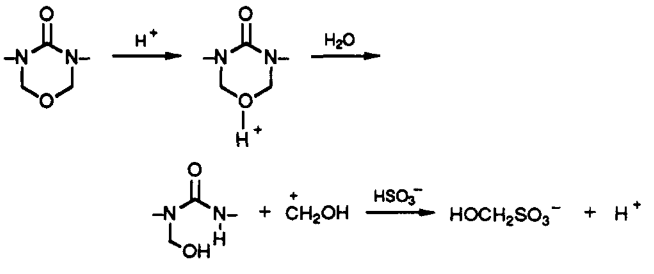
The assignment of the new signals appearing after the sulfonation step has been discussed earlier in detail.[1,2] Differences between structures resulting from following this protocol and the ASC protocol will be highlighted here.

Sulfonation of methylol groups occurs to a lesser extent than the ASC case. The degree of sulfonation (ds) in the ASC case was 100%,[2] whereas in this (ACS) case it varied between 70 and 90%. For S/U of 0.5 the ds was 90%, whereas for the S/U ratio of 1.0 the ds was 70%. However, both the ASC and the ASC protocols resulted in small amounts of $>NCH_2SO_3^-$ (linear and cyclic).

The most significant changes occurring in the reaction mixture and that can be seen from the ^{13}C NMR signals are (a) the decrease in the concentration of the $-CO-$ cyclic, $-CH_2OCH_2-$ cyclic, and the $-CH_2OH$ cyclic groups and (b) the increase in the concentration of the $>NCH_2O-$. The former change was observed in the ASC case; however, the latter was not. It was postulated earlier[2] for the ASC case that the reaction

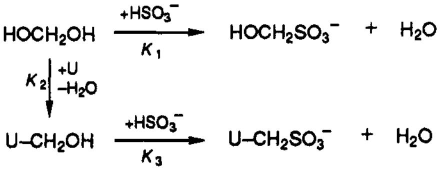


took place but, since there is no appreciable increase in the concentration of the $>NCH_2SO_3^-$ groups for the ACS case, the above explanation does not hold. It is hypothesized that the following reactions occurred:



Effect of the Reaction Order on the Structure of the SUF Resin. Table IV compares the concentration of functional groups in SUF resins prepared according to ASC and ACS protocols. In both preparation procedures only minor amounts of dimethylene ethers are present, and the concentrations of the $>NCH_2OH$ groups are about the same. However, there are differences in structure resulting from the variations in the preparation protocol. One important difference is in the degree of sulfonation. The ASC protocol resulted in a 100% sulfonation whereas the ACS protocol led to 70–90% sulfonation. Another important difference is in the degree of condensation (n). The amount of methylene bridges is significantly higher in the ACS protocol. There is an average of a 20% increase in n (Table IV) when the preparation protocol is changed from ASC to ACS, for the same reactant ratios and reaction conditions. The numbers shown in Table IV are obtained from the data on the concentration of the $-CH_2-$ groups. Theoretically speaking, both the methylene and the dimethylene ether linkages should be considered. However, in both the ASC and ACS, the $-NHCH_2O-$ groups are not present.

Two-Step ASC Protocol. When urea, formaldehyde, and sulfite are reacted in a single step, the relative velocities of the urea–formaldehyde and the formaldehyde–sulfite reactions are expected to affect the behavior of the reaction mixture. It is known from previous experiments that formaldehyde may react with urea and with sulfite in competitive reactions.



Although the formation of methylolureas is a very fast reaction (K_2 is high), free formaldehyde is always present in the reaction mixture and, therefore, the structure of the reaction product, resulting from a two-step ASC protocol, depends on the ratio of K_1 to K_3. In the case where K_3 is much higher than K_1 ($K_3 \gg K_1$), similar chemical structures can be expected from a two-step and three-step ASC protocol. In the case where $K_3 \leq K_1$ or K_3 is slightly higher than K_1, different reaction products have to be expected.

Four resins with F/U = 2.0 and 3.0 and S/U = 0.5 and 1.0 were prepared in a two-step ASC protocol in which the addition and the sulfonation steps were combined in one step. For brevity, only one of these four resins will be compared to a resin prepared in a three-step ASC procedure. Figure 1 compares the NMR spectra of resins prepared in two step (a) and three-step ASC (b) protocols. A close agreement was obtained for the concentration of the various functional groups that are in the reaction mixtures after the end of the addition and sulfonation reactions. A similar agreement was found for all other resins prepared. Table V presents the concentration of the major structural units found in the reaction mixtures of resins prepared in two-step and three-step ASC protocols. The same conclusion regarding the similarity of structures obtained when combining or separating the addition and sulfonation steps is reached.

Conclusions

The sequence of the reaction's steps has a significant effect on the chemical structure of the sulfonated urea–formaldehyde resins. It was shown that when the order of the condensation and sulfonation steps is reversed, several changes in the structure of SUF resins were observed. The degree of sulfonation for the ASC protocol was 100%, whereas for the ACS protocol it was 70–90%. The decrease in the number of sulfonate groups has an important effect on the performance of the resin for a particular application. The degree of condensation (and therefore, the molecular weight of the resin) was higher for ACS protocol. Again, the effect of the molecular weight of a polymer on its properties and performance has been well-documented in the literature.[5] As for branching in the SUF resins, it looks like the ACS protocol leads to less branched structures (Table IV, small amounts of -N< are formed); however, this point needs further verification.

Another major variable investigated in this work was the effect of combining the addition and sulfonation steps in one step. It was demonstrated that two-step and three-step ASC protocols led to very similar products.

The above findings have several significant implications for any product development work conducted on sulfonated amine–formaldehyde resins. First, they provide a means for controlling the degree of condensation and thus the molecular weights of the resins. Second, they can be used to control the degree of sulfonation of a particular resin. Our future publications will illustrate how such information was used in producing SUF resins with certain characteristics for a particular application. Third, the above finding on the "equivalence" of the two-step and three-step ASC protocols can be used to eliminate one step of the reaction procedure. On a commercial production scale, this means time and cost savings and a more economical and profitable operation.

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