Optimization and Characterization of Polyphosphate Fertilizers by Two Different Manufacturing Processes

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ABSTRACT: To explore how different reaction parameters affect the major features of short-chain ammonium polyphosphate (APP) fertilizers, a batch of manufacturing experiments were conducted under two different manufacturing processes [phosphoric acid (PA)−urea and monoammonium phosphate (MAP)−urea]. The APP features including polymerization degree, polymerization rate, solubility, and N and P recovery rates were significantly varied and influenced by the molar ratio of raw materials (P:N), reaction temperature, time, and pressure under different manufacturing conditions. In the MAP−urea process, the optimized APP products were gained under the combination condition of molar ratio = 1.6:1, T = 130 °C, and t = 45 min, while this happened in molar ratio = 1:1.7, T = 180 °C, and t = 60 min in the PA−urea process. Comprehensively, the features of APP fertilizers produced by the MAP−urea process were better than those produced by the PA−urea process. Our results provide valuable references for manufacturing high-quality short-chain APP fertilizers.
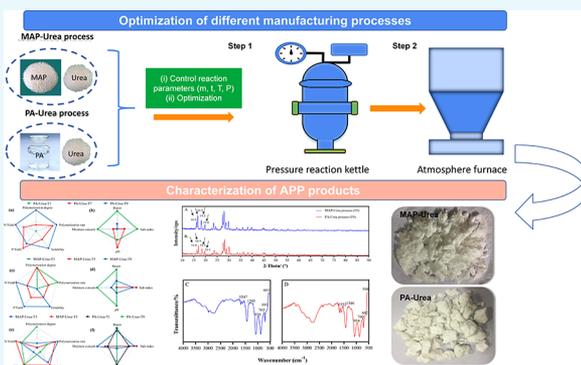
INTRODUCTION

Ammonium polyphosphates (APPs) have long and extensively been used as fire retardants, fire extinguishing agents, food additives, and so on.[1,2] In recent years, short-chain APPs, as an alternative source of effective phosphate fertilizers, have been increasingly applied to agriculture to increase soil P availability and improve phosphorus fertilizer use efficiency (PUE).[3,4] In general, when poly-P is applied to soil, it cannot be directly taken up by plants[5] until gradually hydrolyzed to ortho-P. The hydrolysis of APP fertilizers largely depends upon its chemical nature and edaphic factors such as pH,[6] soil texture, and soil temperature.[7] Some studies showed that short-chain soluble polyphosphate fertilizers (2 < n < 20) out-competed orthophosphate-based fertilizers [i.e., monoammonium phosphate (MAP), diammonium phosphate(DAP), and triple superphosphate (TSP)] in increasing soil available P[7,8] and improving crop yield and PUE.[4] Because polyphosphate possesses slow-releasing characteristic,[9] APP application significantly reduced soil P fixation,[10] and increased soil P availability.[11] Apart from this, poly-P fertilizers also exhibit significant effects on mobilizing or activating soil recalcitrant P through chelating with soil metal ions (Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}).[4,12] Therefore, applying poly-P fertilizers in agriculture has attracted great attention.

Chemically synthesized polyphosphate fertilizers consist of polyphosphate (poly-P) and orthophosphate (ortho-P) at a given proportion. Conceptually, the polymerization degree (n, the average chain length of phosphate molecule in APP) and polymerization rate (percent of poly-P accounting for total-P

in APP) of APP are considered as two critical factors.[13] Both of them significantly influence the solubility and hydrolysis of poly-type P fertilizers; they also significantly impacted the chemical behaviors of poly-P fertilizers in soils.[4] For example, the solubility and hydrolysis rate of poly-P fertilizers decreased with the polymerization degree increase.[14] Basically, the hydrolysis of poly-P fertilizers occurs through sequentially decreasing the polymerization degree from poly-P ($n > 4$) to tetraphophosphate ($P_4O_{13}^{6-}$) to tripolyphosphate ($P_3O_{10}^{5-}$), then to pyrophosphate ($P_2O_7^{4-}$), and finally to orthophosphate (PO_4^{3-}).[15] On the other hand, the polymerization rate, as an important parameter of poly-P fertilizers, significantly influenced soil P bioavailability and P fixation.[4] These two parameters are mainly affected by different manufacturing processes and the corresponding fabricating reaction parameters.[16,17]

Up until now, PA−urea and MAP−urea are two mainstream manufacturing processes used for producing poly-P fertilizers.[18,19] In general, the features of APP fertilizers, including polymerization degree, polymerization rate, solubility, biuret content, pH, and salt index, are vital important parameters
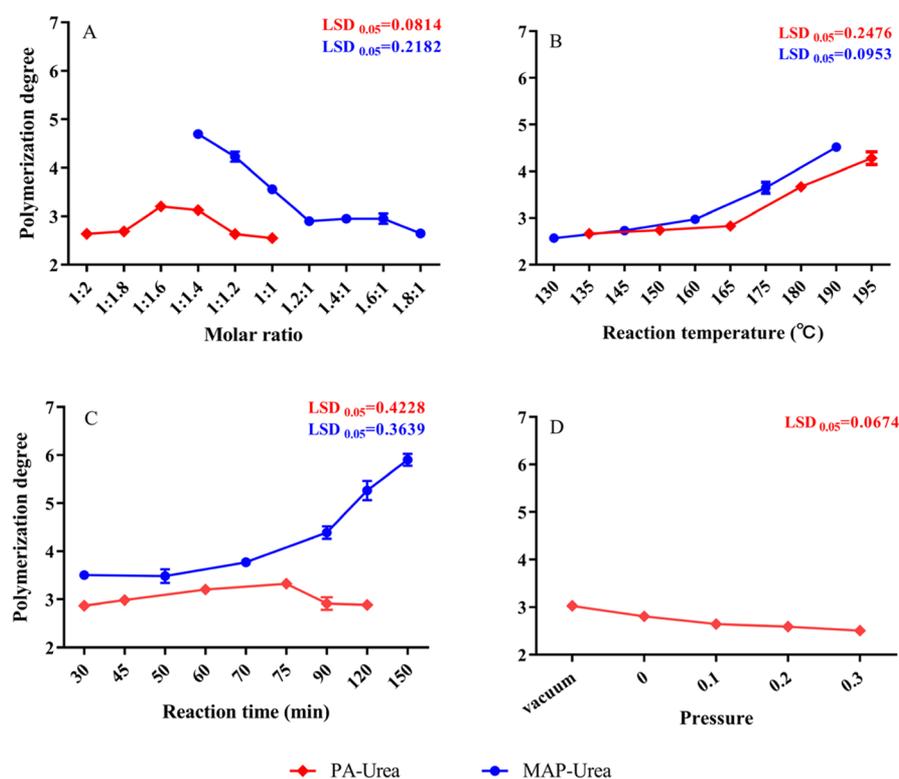
Figure 1. Influences of substrates' molar ratio (a), reaction temperature (b), reaction time (c), and pressure (d) on the polymerization degree of APP (single-factor experiment). Note: Data are mean ± standard deviation (SD), $n = 4$. Bars represent the average standard deviation of the means.

used to evaluate the quality of the APP fertilizers.[20] APP manufacturing conditions not only affect the features of APP but also affect the appearance of the product.[17,21] Moreover, N and P recovery rates are regarded as important parameters to assess the performance of APP manufacturing processes. All these are directly influenced by different manufacturing processes and reaction conditions (molar ratio of raw materials, reaction time, temperature, and pressure). However, knowledge about how different manufacturing process conditions influence the features and quality of APP fertilizers is not well-established yet, and the published literature about the optimized short-chain APP fabricating parameters is rarely available.

In this study, two contrasting pilot-scale manufacturing processes of PA−urea and MAP−urea were compared to investigate the influences of different manufacturing conditions on the features of short-chain APP fertilizers. Therefore, the specific objectives of the current study were to (i) explore responses of the features of the short-chain APP products to different manufacturing conditions (molar ratio of raw materials, temperature, reaction time, and pressure) and (ii) optimize short-chain APP fertilizers' fabricating process and further evaluate the effects of different manufacturing processes on the features of the short-chain APP. Our outcomes will provide valuable information in optimizing short-chain APP manufacturing processes and will be helpful to put forward the development of polyphosphate-containing fertilizers' production technology.

■ RESULTS

Polymerization Degree of APP. The polymerization degree (n) of APP was significantly affected by the molar ratio of raw materials, reaction temperatures, times, and pressures.

In the MAP−urea manufacturing process, the polymerization degree decreased from 4.7 to 2.9, with the molar ratio of $[NH_4H_2PO_4]:[CO(NH_2)_2]$ increasing from 1:1.4 to 1.2:1 (Figure 1a) ($p < 0.05$). Similarly, within the given ranges of reaction time (30−150 min) and temperature (130−190 °C), the polymerization degree increased with the increase of these two reaction conditions (Figure 1b,c).

In the PA−urea manufacturing process, the polymerization degree increased to the peak value of 3.2 at the $[H_2PO_3]$:$[CO(NH_2)_2]$ molar ratio of 1:1.6 and then decreased with the increase of the molar ratio of $[H_2PO_3]$:$[CO(NH_2)_2]$ (Figure 1a). With the increase of reaction temperature, the polymerization degree steadily increased from 2.7 to 4.3. However, reaction pressure adversely affected the polymerization degree (Figure 1d). The highest value of the polymerization degree occurred at a reaction time of 75 min across all reaction times (Figure 1c). Comparatively, a higher value of polymerization degree always happened in MAP−urea rather than in PA−urea manufacturing processes, and the influences of the molar ratio of raw materials, reaction temperature, and time on the polymerization degree were more pronounced in MAP−urea than in PA−urea manufacturing processes.

Polymerization Rate of APP. As shown in Figure 2, the molar ratio of raw materials, reaction temperature, time, and pressure significantly influenced the polymerization rate of APP. In general, the polymerization rate decreased with the increase of the molar ratio from 1:2 to 1:1.4 in both two APP manufacturing processes (Figure 2a); it also decreased with the increase in reaction pressure (Figure 2d). In contrast, the polymerization rate increased with the increase of reaction time and temperature (Figure 2b,c). In addition, the average value of the polymerization rate was consistently significantly greater in MAP−urea than in PA−urea processes. For instance,
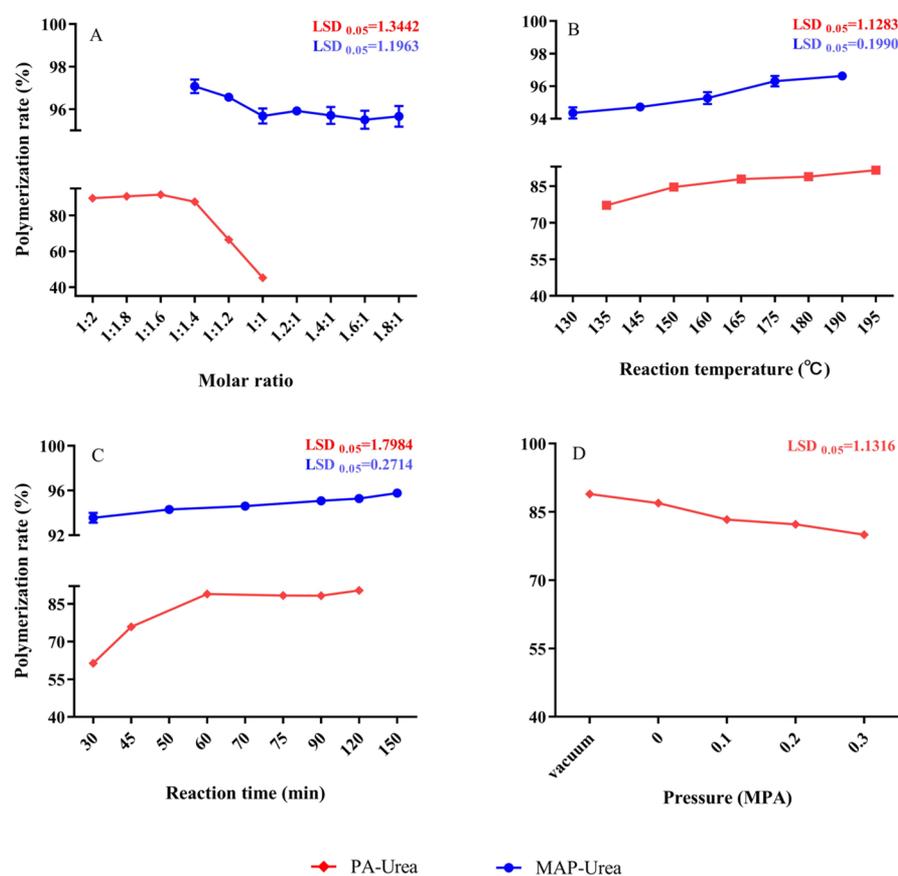
Figure 2. Influences of substrates' molar ratio (a), reaction temperature (b), reaction time (c), and pressure (d) on the polymerization rate of ammonium polyphosphate (single-factor experiment). Note: Data are mean ± standard deviation (SD), $n = 4$. Bars represent the average standard deviation of the means.

the averaged polymerization rates across reaction time and temperature were 95.5 and 94.7%, respectively, in the MAP−urea process, which were 10.2 and 15.3% higher, respectively, than in the PA−urea manufacturing process.

N and P Recovery Rates of APP. N and P recovery rates of APP notably varied with different reaction conditions in both MAP−urea and PA−urea manufacturing processes (Figure 3a−h). N recovery rates decreased with the increase of reaction temperature and time, with the average values of 63.3 and 69.7% in the MAP−urea process, respectively, which were 62.9 and 71.1% in the PA−urea process. In addition, in the MAP−urea process, the N recovery rate increased with the increase of the molar ratio, but the opposite trend was true in the PA−urea manufacturing process. Similar observations also happened for the P recovery rate in both MAP−urea and PA−urea manufacturing processes (with exception of reaction pressure).

Solubility of APP. APP solubility increased with the increase of the molar ratio, and the highest values of APP solubility were gained at molar ratios of 1.8:1 and 1:1.2, respectively, in MAP−urea and PA−urea manufacturing processes (Figure 4a). With the increase in reaction temperature and time, APP solubility showed a decreasing trend in the MAP−urea process, but it showed an increasing trend in the PA−urea process (Figure 4b,c). Collectively, reaction conditions of a high molar ratio of raw materials together with low reaction temperature, reaction time, and pressure favored the APP fertilizer to have high solubility.

Orthogonal Test Experiment. Based on the optimal reaction parameters obtained from the single-factor experiment, an orthogonal test experiment was conducted to comprehensively compare the influences of different optimized parameter combinations on the features of APP products. As shown in Tables 1 and 2, in the MAP−urea process, the influences of different reaction factors for the polymerization degree followed the order of molar ratio (n) > reaction time (t) > temperature (T), while for solubility, it followed order of $t > n > T$. Hence, for the polymerization degree, the optimized manufacturing combination condition was $A_1B_3C_3$ (molar ratio = 1.5:1, $T = 140$ °C, and $t = 45$ min), while it was $A_3B_2C_2$ for solubility (molar ratio = 1.7:1, $T = 130$ °C, and $t = 30$ min) (Table 1).

Likewise, in the PA−urea process, the influences of different reaction factors for the polymerization degree followed the order of $n > t > T$; the optimized combination was $A_3B_3C_2$ (molar ratio = 1:1.7, $T = 180$ °C, and $t = 60$ min) for the polymerization degree. Regarding APP solubility, the influences of different reaction factors followed the order of $T > t > n$, and $A_3B_3C_3$ was the optimized combination (molar ratio = 1:1.7, $T = 180$ °C, and $t = 75$ min) for APP solubility (Table 2).

Moreover, the Radar chart showed that the relative high polymerization degree, N and P recovery rate, and solubility, together with low moisture content, burient content, and salt index occurred under the combination condition of molar ratio = 1.6:1, $T = 130$ °C, and $t = 45$ min (T5) for the MAP−urea manufacturing process, while for the PA−urea manufacturing

● PA−Urea   ● MAP−Urea
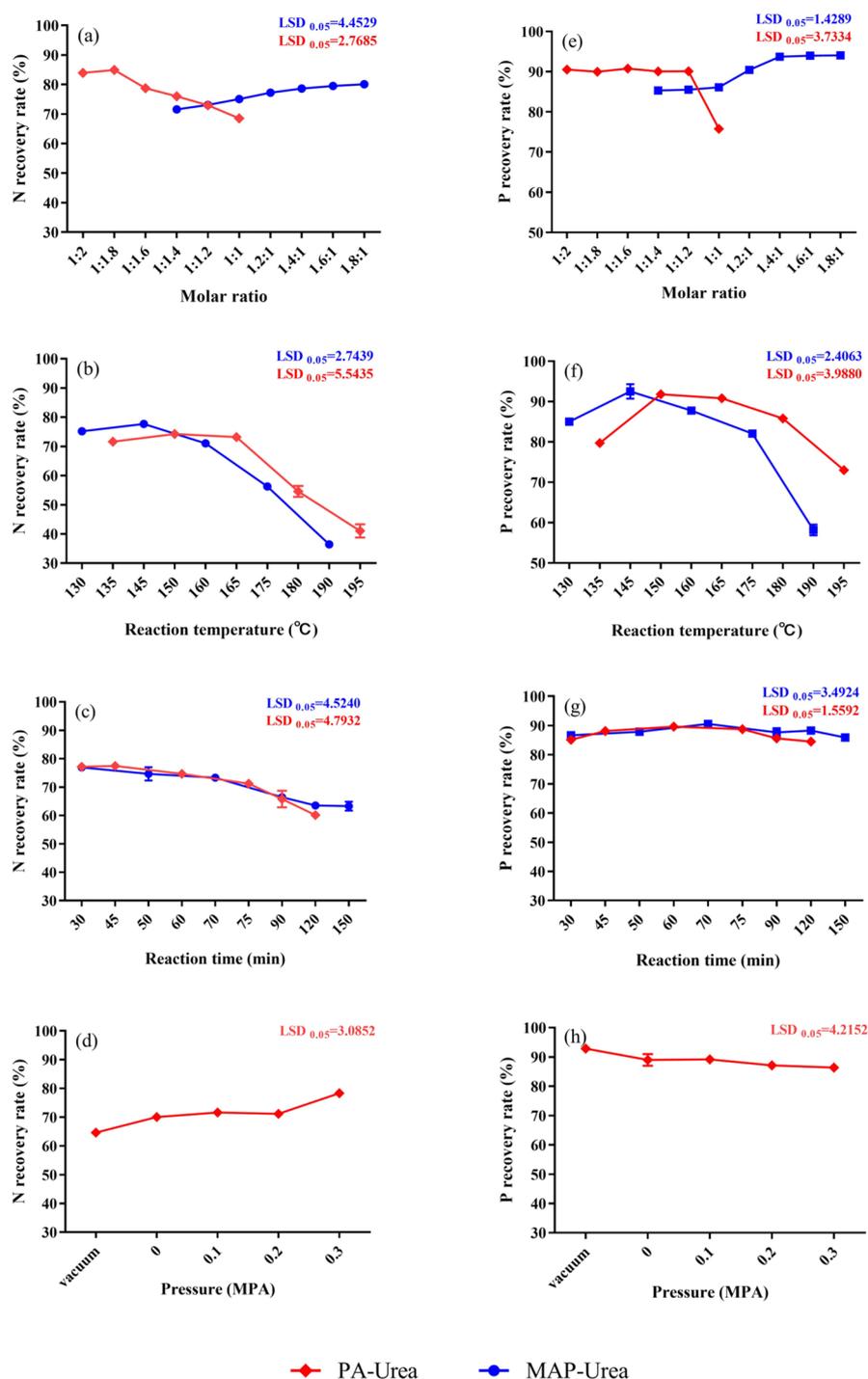
Figure 3. Influences of substrates' molar ratio (a and e), reaction temperature (b and f), reaction time (c and g), and pressure (d and h) on the N and P recovery rates of ammonium polyphosphate (single-factor experiment). Note: Data are mean ± standard deviation (SD), $n = 4$. Bars represent the average standard deviation of the means.

process, that happened in the combination condition of molar ratio = 1:1.7, $T = 180$ °C, and $t = 60$ min (T9) (Figure 5).

■ **DISCUSSION**

Both PA−urea and MAP−urea manufacturing processes have been commonly used to manufacture APP fertilizers.[22] In this study, the X-ray diffraction (XRD) method with Cu Kα radiation ($\lambda = 1.542$ Å) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the crystal shape of the produced APP product (Figure 6). When

compared to the standard reference, XRD spectra showed that there were three diffraction peaks near 16−18°, and no diffraction peaks occurred between 20 and 23° (Figure 6a,b). This indicated that the APP products fabricated by the optimized MAP−urea and PA−urea processes both belonged to APP-I with a linear structure.[23] The FTIR spectra of APP products are shown in Figure 6c,d. The synthesized APP products have absorption peaks near 760 cm^{-1} (O=P−O), 682 cm^{-1} (−OH), and 600 cm^{-1} (O−P−O). These absorption peaks were regarded as the characteristic of
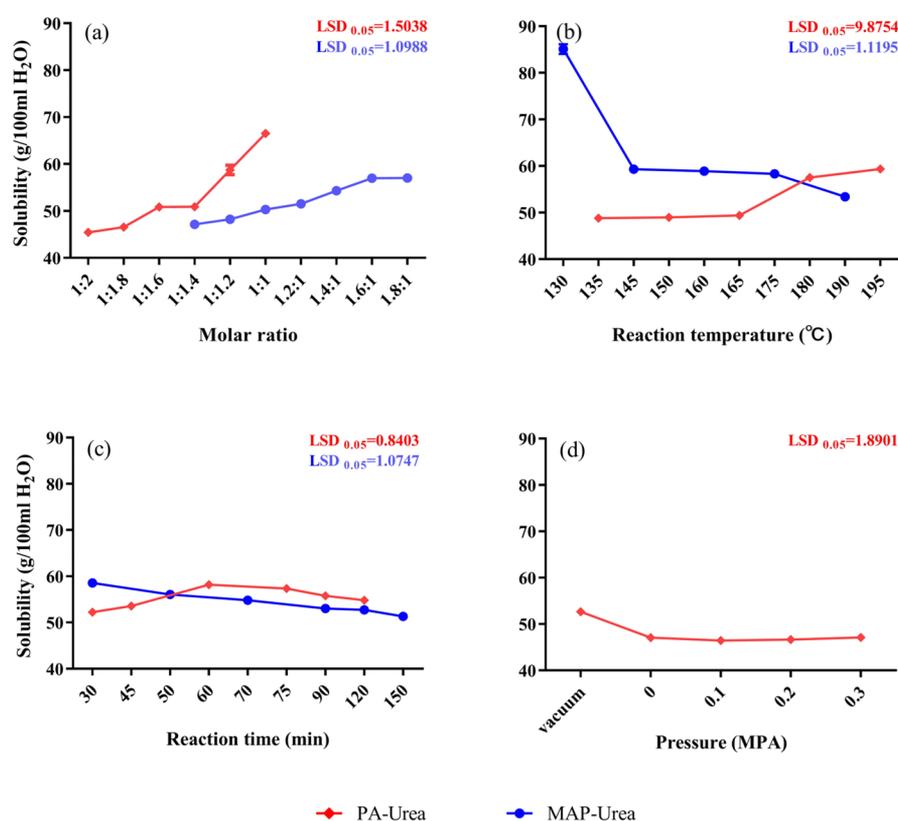
Figure 4. Influences of substrates' molar ratio (a), reaction temperature (b), reaction time (c), and pressure (d) on solubility of ammonium polyphosphate (single-factor experiment). Note: Data are mean ± standard deviation (SD), $n = 4$. Bars represent the average standard deviation of the means.

Table 1. Comprehensive Analysis of Different Factors Affecting Key Parameters of Ammonium Polyphosphate Fabricated by the MAP−Urea Process Using the Comprehensive Balance Method

counting projects		factor level			index	factors	optimum
		Amolar ratio	Btemperature	CTime	sums	order	programmer
polymerization degree	k1	2.82	2.77	2.66	$\sum = 8.29$	ACB	$A_1B_3C_3$
	k2	2.86	2.77	2.84			
	k3	2.61	2.76	2.79			
	R	0.25	0.01	0.18			
polymerization rate (%)	k1	97.0	95.6	96.6	$\sum = 290.6$	BCA	$A_1B_3C_3$
	k2	96.8	97.4	95.6			
	k3	96.8	97.7	97.5			
	R	0.24	2.11	0.89			
solubility (g/100 mL H_2O)	k1	79.8	81.6	85.1	$\sum = 246.1$	CAB	$A_3B_2C_2$
	k2	81.1	83.3	81.0			
	k3	85.2	81.2	79.9			
	R	5.36	2.16	5.1			
P recovery rate (%)	k1	89.9	86.9	91.9	$\sum = 269.3$	ABC	$A_2B_2C_3$
	k2	92.7	92.6	87.9			
	k3	86.7	89.9	89.6			
	R	5.95	5.73	4.1			
N recovery rate (%)	k1	82.2	81.8	87.4	$\sum = 253.9$	ABC	$A_2B_3C_1$
	k2	89.0	86.8	82.8			
	k3	82.7	85.3	83.7			
	R	6.85	5.0	4.52			

absorption peaks of APP-I,[24] which further evidenced that the manufactured APP products in this study were identified as APP-I. However, the APP fertilizers produced by two different manufacturing processes showed some differences in appearance. For example, as the APP fertilizers are produced by the MAP−urea process, the APP products had a whiter color with a crisper texture, but APP produced by the PA−urea process showed a yellowish color with a harder texture ([Figure 7](#)). In addition, the polymerization degree of APP produced by the MAP−urea process was significantly higher than that in the

Table 2. Comprehensive Analysis of Different Factors Affecting Key Parameters of Ammonium Polyphosphate Fabricated by the PA−Urea Process Using the Comprehensive Balance Method

counting projects		factor level			index	factors	optimum
		Amolar ratio	Btemperature	Ctime	sums	order	programmer
polymerization degree	k1	2.91	2.86	2.90	$\sum$ = 9.12	ABC	$A_3B_3C_2$
	k2	2.86	3.02	3.17			
	k3	3.34	3.24	3.04			
	R	0.48	0.39	0.27			
polymerization rate (%)	k1	91.9	89.8	92.3	$\sum$ = 276.8	BCA	$A_3B_3C_2$
	k2	92.1	93.2	93.3			
	k3	92.8	93.8	91.3			
	R	0.93	4.01	1.99			
solubility (g/100 mL H_2O)	k1	49.0	46.2	47.5	$\sum$ = 147.5	BCA	$A_3B_3C_3$
	k2	48.5	49.9	49.7			
	k3	49.9	52.3	50.2			
	R	1.49	2.69	2.69			
P recovery rate (%)	k1	81.9	89.9	87.8	$\sum$ = 259.7	BAC	$A_2B_1C_1$
	k2	90.5	89.0	86.5			
	k3	87.3	79.8	84.4			
	R	8.6	10.1	3.4			
N recovery rate (%)	k1	56.7	70.6	71.9	$\sum$ = 203.4	ACB	$A_3B_1C_1$
	k2	68.6	69.4	69.3			
	k3	78.1	63.3	62.2			
	R	21.4	7.26	9.71			

PA−urea process; this result was similar to that reported by Bai et al. (2016).[25] Therefore, different reaction parameters, such as the molar ratio of raw materials, temperature, reaction time, and pressure, exerted significant influences on the features of APP samples (polymerization degree, polymerization rate, solubility, and N and P recovery rates). On the other side, inappropriate manufactory parameters will lead to a serious dissolution recrystallization and excess of water-insoluble substance problems.[17,18]

During the APP manufacturing process, the condensed P fertilizers with a P-O-P alternating structure are formed by dehydration of orthophosphate.[26] In this study, raw materials' molar ratio showed more obvious influence on the polymerization degree in the PA−urea process than in the MAP−urea process (Figure 1a). Actually, many factors can affect the feature, purity, and quality of the APP fertilizers, such as type of different raw materials, purity, and dewatering efficiency in the reaction process and crystal size distribution.[27] We considered that water inhibition may be the most important reason. One possible explanation is that, when excess free water was present in phosphoric acid, a large amount of exhaust gas discharged during the APP manufacturing process. This made the reactants sticky and foamy, which further affected the continuous APP fabricating process. Another explanation may be that excess water affects polymerization reaction under acidic conditions.[25] Besides, our findings showed that the polymerization degree and polymerization rate significantly decreased with the increase of the molar ratio (P:N) (Figure 1a, Figure 2a, and Figure 3a,b), especially in the PA−urea process. This also partially implied that polymerization reaction was inhibited due to the presence of excess water. Moreover, in both PA−urea and MAP−urea manufacturing processes, urea not only acts as a dehydration condensation agent (urea combined with water produced by phosphoric acid (PA) or monoammonium phosphate (MAP) dewatering promotes the dehydration reaction occurrence), but also plays an important role in breaking the P−O−NH$_4^+$

bond of MAP and lowers its activation energy.[28] Therefore, the addition of urea with a proper dose is a prerequisite to obtain high-quality APP products.[17] For example, when the amount of urea is not sufficient, the polymerization reaction cannot be completed, and thus, the polymerization degree is low: $nH_3PO_4 + (n-1)CO(NH_2)_2 \rightarrow (NH_4)_n + 2P_nO_{3n+1} + (n-4)NH_3\uparrow + (n-1)CO_2\uparrow$.[28] Reversely, excessive input of urea makes the produced APP product quite sticky, which makes it difficult to form a crystallization structure. Besides, our findings showed that the polymerization degree, polymerization rate, and N and P recovery rates of APP significantly decreased with the increase of the molar ratio (P: N) (Figure 1a, Figure 2a, and Figure 3a,b), especially in the PA−urea process. This phenomenon may be caused by the presence of water on the one hand. On the other hand, when the molar ratio of P: N is greater than 1:1.4 in the PA system and 1:1.1 in the MAP system, the amount of urea is not enough to carry out condensation polymerization.

The APP manufacturing process can be divided into heating → melting → polymerization (a small amount of crystal conversion). Previous studies showed that reaction time significantly impacted the polymerization degree of APP. The polymerization reaction cannot commence until the raw materials were totally melted. The polymerization degree of APP initially increased and then showed a decreasing trend with the increase of reaction time.[29] This result was consistent with our findings. As such, when shortening the reaction time, the polymerization degree is low because the reaction does not approach equilibrium; hence, a large fraction of oligomeric APP, rather than polypolymeric APP, is yielded. However, when prolonging the reaction time, more side reaction such as degradation of APP easily happened. He et al. (2009) indicated that over 50% of polymerization was completed after 5 min of reaction time and 90% after 12 min of reaction time.[30] In this study, we found that the transformation of raw materials from the molten phase to solid phase took only 2−3 min. This suggested that polymerization mainly happened in the first step
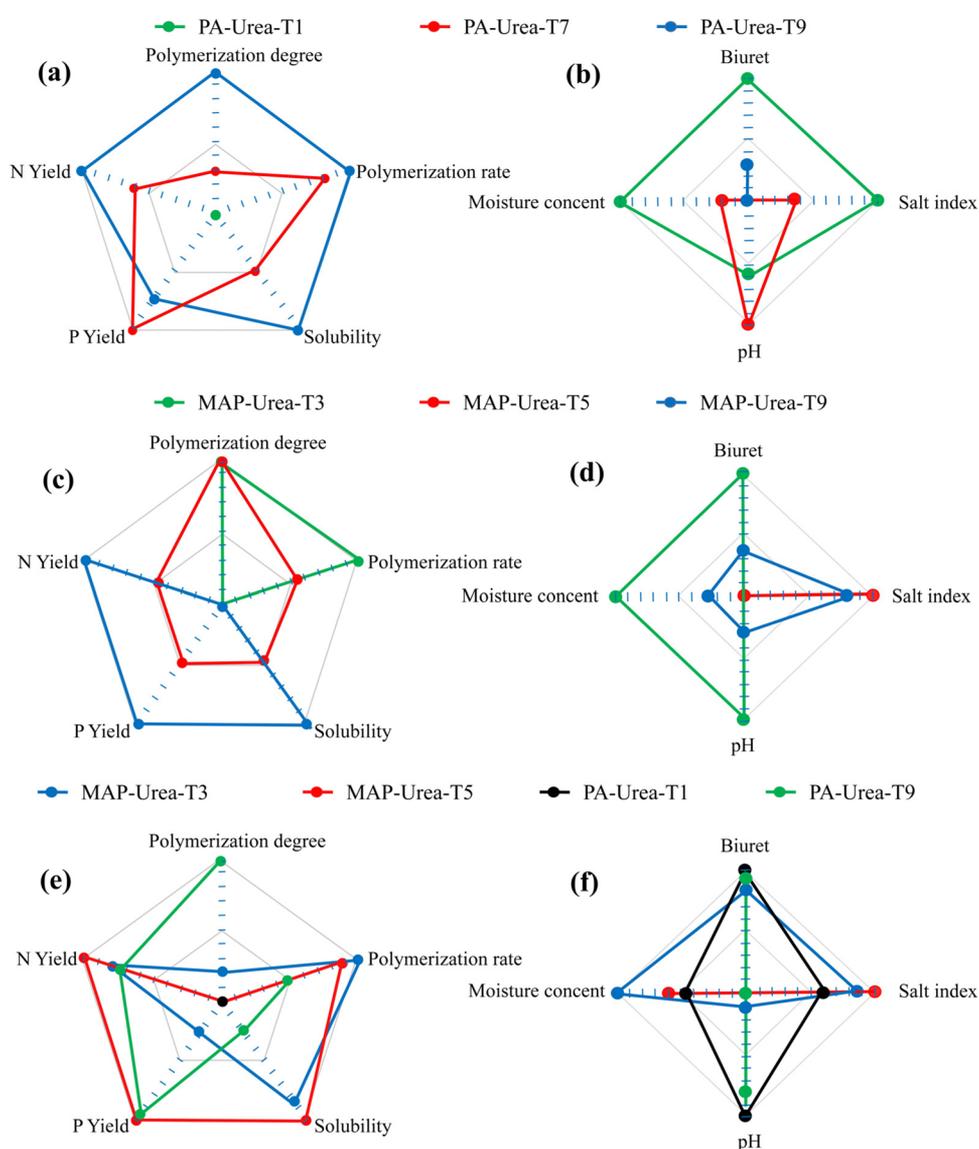
Figure 5. Radar chart analyzing the influences of different manufacturing factors on key parameters (a), (c), and (e) and other indicators (b), (d), and (f) of ammonium polyphosphate. Note: The value of 0 represents the worst outcome, and the value of 1 represents the best outcome (min−max normalization was performed to normalize data to a range of 0 to 1, and the formula was $x^* = (x - \min)/(\max - \min)$) in the radar chart.

of the synthesis of APP, and the elongation of the P-O-P chain primarily occurred in the second step.

Temperature is another major factor affecting the quality of the produced APP. As such, the number of polymers (polymerization degree) increased with reaction temperature. However, the polymers can only accomplish dehydration reaction and appear as the solid phase when thermocondition requirement (reaction temperature) cannot be totally satisfied. In this study, we found that when the temperatures reached up to 190 and 195 °C, the highest polymerization degree and polymerization rate (Figure 1b and Figure 2b) were achieved in MAP−urea and PA−urea manufacturing processes accordingly. Moreover, reaction temperature increasing gradient (heating rate) significantly affected the occurrence of the side reaction of urea decomposition[31] and deamination of urea.[32] We found that a side reaction occurred, when reaction temperature exceeded 180 °C, and it caused material overmelting and APP products were stratified. As a result, solid APP products appeared on the top of the reaction vessel, but on the bottom of the reaction vessel, APP products

appeared as a transparent sticky colloid substance. This phenomenon may result in a significant reduction in the N and P recovery rate. In this study, the temperature increasing gradient was set as 3 °C/min to avoid production of melamine and prevent activating polymerization reaction before the substrates are melted completely.[26] On the other hand, the temperature of the polycondensation reaction can be reduced by urea addition. In this case, the polymerization reaction is inhibited, and the oligomer APP cannot be converted to a higher polymerization degree of polymeric APP. Additionally, the extreme reaction temperature is limited to avoid the reaction material spilling out of the polymerization reactor and corroding equipment.[33] The solubility of the APP products showed an opposite trend with the polymerization degree; it decreased with the increase of reaction time and temperature (Figures 1 and 4). Collectively, in this study, we have offered some pragmatic and useful information on how different manufacturing processes and production parameters influence the major features of short-chain APP fertilizers. When considering agriculture fertilization practices, we suggest that
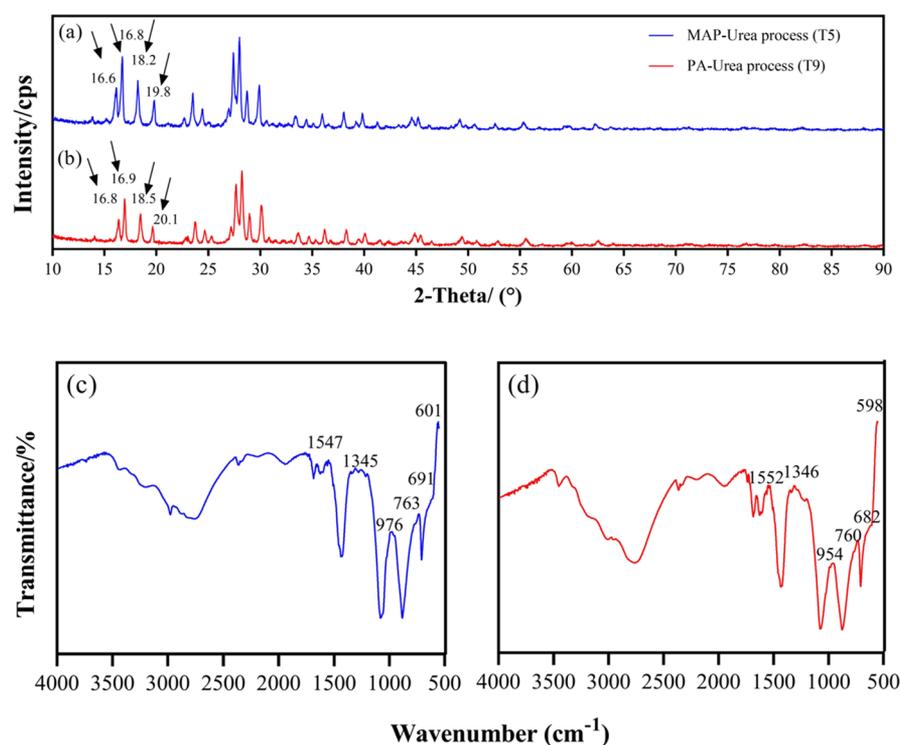
Figure 6. XRD (a and b) and FTIR (c and d) spectroscopic characterizing ammonium polyphosphate samples fabricated in this study.
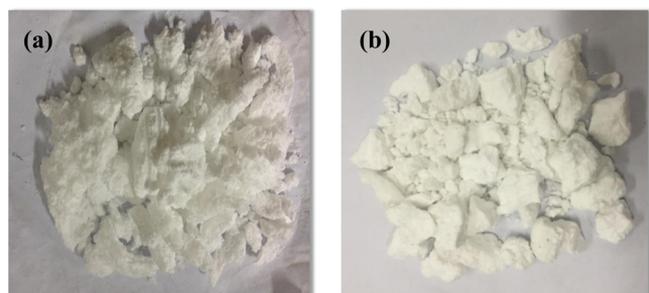
Figure 7. Ammonium polyphosphate products fabricated by the MAP−urea process (a) and PA−urea process (b).

it is necessary to regulate these parameters such as the molar ratio of raw materials, reaction temperature, time, and pressure to form a proper APP fertilizer formula based on soil type and the basic physiochemical condition of the soil; also, the cultivation pattern and fertilization methods in different regions should be taken into account to improve the agronomic performance of APP fertilizers and the efficiency of P fertilizer use.

CONCLUSIONS

In summary, the major features of APP such as the polymerization degree, polymerization rate, solubility, and N and P recovery rates were significantly affected by the reaction parameters such as the molar ratio of raw materials, reaction temperature, time, and pressure under both PA−urea and MAP−urea fabricating conditions. The increases in reaction temperature and time within a certain range were found to be beneficial to the APP polymerization degree and polymerization rate increase, but these were unfavorable to solubility and N and P recovery rates. Moreover, the influences of major reaction parameters on the features of APP varied differently in

different manufacturing processes. In the PA−urea process, the optimized condition was molar ratio = 1:1.7, T = 180 °C, and t = 60 min for the polymerization degree and molar ratio = 1:1.7, T = 180 °C, and t = 75 min for solubility; while in the MAP−urea process, the optimized condition was molar ratio = 1.5:1, T = 140 °C, and t = 45 min for the polymerization degree and molar ratio = 1.7:1, T = 130 °C, and t = 30 min for solubility. Comparatively, the APP polymerization degree produced by the MAP−urea process was significantly higher than that produced by the PA−urea process. Taken together, our results demonstrated that the optimized MAP−urea manufacturing process was superior to the PA−urea process in fabricating short-chain APP. Therefore, to achieve the best agronomic effectiveness, soil type, soil physicochemical properties, cultivation pattern, and fertilization methods must be taken into account when designing and optimizing the short-chain APP fertilizer manufacturing process and parameters.

EXPERIMENTAL SECTION

Experimental Materials. Pilot-scale fabrication of short-chain APP was carried out by using two different manufacturing processes: (i) MAP−urea process and (ii) phosphoric acid-urea (PA−urea process). For the PA−urea manufacturing process, phosphoric acid and urea were used as raw materials to synthesize APP; while for the MAP−urea process, MAP and urea were employed to produce APP. Three analytical pure reagents used as raw materials in this study were MAP (MAP, 99.9% purity, P_2O_5 61.7%) and urea ($N \geq$ 46.7%), provided by the Shengao chemical plant (Tianjin, China), and PA (P_2O_5 61.6%, Laboratory reagent), provided by Aladdin Reagent Co. (Shanghai, China). The manufacturing equipment used in this study is shown in Figure 8.

APP Fabrication Process. The pilot-scale fabrication of the APP fertilizer by PA−urea and MAP−urea processes is
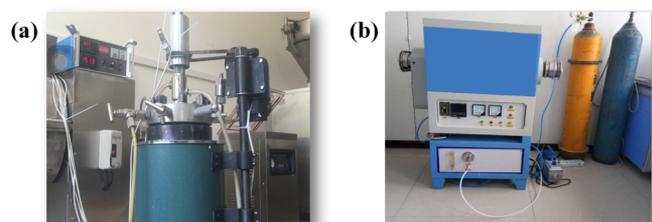
Figure 8. Diagram of equipment for the production of APP fertilizers: (a) 2 L pressure reaction kettle used for step 1 and (b) 5 L atmosphere furnace used for step 2.

shown in Figure 9. Basically, the APP fabrication process can be divided into two steps: pre-polymerization stage and
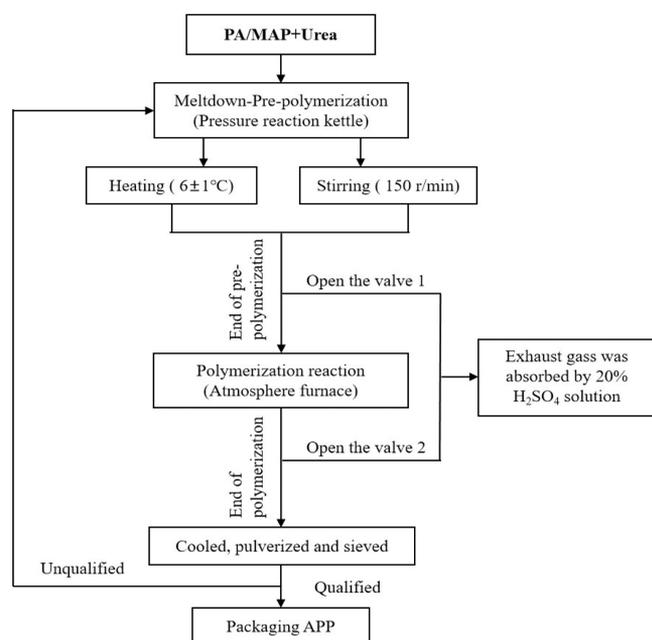
Valve 1: exhaust valve of the GSH-high pressure reactor;
Valve 2: exhaust valve of the atmosphere furnace.

Figure 9. Schematic diagram of the processes used for fabricating ammonium polyphosphate.

polymerization stage. For the first step (pre-polymerization stage), the analytical pure grade PA or MAP was mixed with urea in a 2-liter pressure reaction kettle (GSH-2 L, Yanzheng experimental instrument Co., LTD, Shanghai, China) at the designed molar ratio of raw materials (Tables 345). Afterward, the mixture was heated at a temperature increasing gradient of 3 ± 1 °C min^{-1} till the temperature reached the setting reaction temperature, and then, this temperature was maintained based on the designed reaction time. During the whole reaction period, the mixture was stirred at a speed of 150 rpm. During this stage, urea gradually melted along with the increase in reaction temperature, the melted urea completely reacted with PA or fine particles of MAP, and then a semi-finished product of APP was produced. In the second step (polymerization stage), the semi-finished product was promptly transferred to a 5-L atmosphere furnace (CR-GJ10, Bolite Electromechanical Co. Ltd., China) to complete the polymerization procedure. In this stage, the water in the mixture was gradually evaporated, and thereafter, phosphate was condensed into the polyphosphate form. Meanwhile, the

Table 3. Single-Factor Design of PA−Urea and MAP−Urea Manufacturing Processes

methods	factor level	molar ratio of P:N (A)	temperature (°C) (B)	reaction time (min) (C)	pressure (MPa) (D)
PA−urea	1	1:2	135	30	vacuum
	2	1:1.8	150	45	0
	3	1:1.6	165	60	0.1
	4	1:1.4	180	75	0.2
	5	1:1.2	195	90	0.3
	6	1:1		120	
MAP−urea	1	1:1.4	130	30	
	2	1:1.2	145	45	
	3	1:1	160	60	
	4	1.2:1	175	75	
	5	1.4:1	190	90	
	6	1.6:1		120	
	7	1.8:1		150	

Table 4. Design of Orthogonal of PA−Urea and MAP−Urea Manufacturing Processes

methods	factor level	molar ratio of P:N (A)	temperature (°C) (B)	reaction time (min)(C)
PA−urea	1	1:1.5	150	45
	2	1:1.6	165	60
	3	1:1.7	180	75
MAP−urea	1	1.5:1	120	15
	2	1.6:1	130	30
	3	1.7:1	140	45

produced exhaust gases (including unreacted ammonia, steam, and CO_2) were recovered by 20% H_2SO_4 solution. Finally, the produced APP sample was air-cooled, pulverized, screened through a 2 mm sieve, and stored in a tightly sealed bottle to prevent moisture.

Experiment I (Single-Factor Experiment). In experiment I, a single-factor experiment was established to investigate the influences of different manufacturing conditions, namely, reaction molar ratio of raw materials (A), temperature (B), reaction time (C), and pressure (D) on the APP fertilizer's polymerization degree, polymerization rate, solubility, and N and P recovery rates under both PA−urea and MAP−urea manufacturing processes. Based on previous research studies[17,19,25,28] and our experiences, the ranges of reaction conditions were determined. In the PA−urea manufacturing process, six different molar ratio levels of $[H_2PO_3]$:$[CO(NH_2)_2]$ ranged from 1:2 to 1:1, five reaction temperature levels varied from 135 to 195 °C, six reaction time levels ranged from 30 to 120 min, and four pressure levels ranged from vacuum to 0.3 MPa. These reaction conditions were independently designed. In the MAP manufacturing process, reaction conditions included six different molar ratio levels of $[NH_4H_2PO_4]$:$[CO(NH_2)_2]$ ranging from 1:1.4 to 1.8:1, five reaction temperature levels ranging from 130 to 190 °C, and six reaction time levels ranging from 30 to 150 min, which were independently designed. Each treatment (reaction condition) was replicated four times. Detailed information is shown in Table 3.

Experiment II (Orthogonal Test Experiment). In experiment II, an orthogonal test experiment was conducted. The optimal reaction conditions were established based on the results obtained from the single-factor experiment (experiment

Table 5. Orthogonal Design Program

treatments	PA−urea			MAP−urea		
numbers	molar ratioA	temperature B (°C)	reaction timeC (min)	molar ratioA	temperature B (°C)	reaction timeC (min)
1	1:1.5	150	45	1.5:1	120	15
2	1:1.5	165	60	1.5:1	130	30
3	1:1.5	180	75	1.5:1	140	45
4	1:1.6	150	60	1.6:1	120	30
5	1:1.6	165	75	1.6:1	130	45
6	1:1.6	180	45	1.6:1	140	15
7	1:1.7	150	75	1.7:1	120	45
8	1:1.7	165	45	1.7:1	130	15
9	1:1.7	180	60	1.7:1	140	30

I) (Table 4). The goal of experiment II was to comprehensively investigate the effects of the combination of optimal single reaction conditions on the features of polyphosphate fertilizers produced by either the MAP−urea or PA−urea process. Three factors (optimized single reaction condition) involved in experiment II were reaction molar ratio (A), temperature (B), and reaction time (C). Detailed information of the factors and their designed levels is given in Table 5. Each treatment was replicated four times.

R1: The reaction of phosphoric acid and urea is shown below (PA−urea process):

$$n\text{H}_3\text{PO}_4 + (n-1)\text{CO(NH}_2)_2$$
$$\rightarrow (\text{NH}_4)_n + 2\text{P}_n\text{O}_{3n+1} + (n-4)\text{NH}_3 \uparrow + (n-1)\text{CO}_2 \tag{1}$$
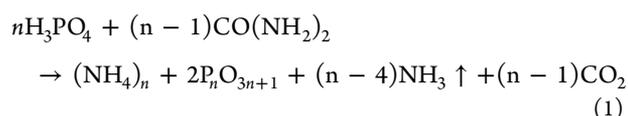
R2: The reaction of MAP and urea is shown below (MAP−urea process):

$$\text{CO(NH}_2)_2 + (\text{NH}_4)\text{H}_2\text{PO}_4 \rightarrow (\text{NH}_4)_4\text{P}_2\text{O}_7 + \text{CO}_2\uparrow \tag{2}$$

$$(\text{NH}_4)_4\text{P}_2\text{O}_7 + \text{CO(NH}_2)$$
$$\rightarrow 2/n(\text{NH}_4\text{PO}_3)_n + 4\text{NH}_3 \uparrow + \text{CO}_2\uparrow \tag{3}$$
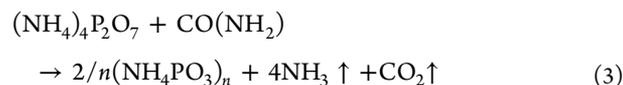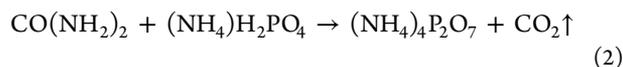
Measurements of the Features of APP Samples. The major features of APP samples, such as polymerization degree, polymerization rate, N and P recovery rates, pH, solubility, and salt index, are assayed using the following methods (more detailed information about determination methods is given in the Supporting Information).

The polymerization degree of APP was determined according to the modified end-group titration method[7,34] with an automatic potentiometric titrator (T-860, Jinan Hanon Instruments Co., Ltd., China). Briefly, 0.5000 g of the APP sample was dissolved with 30 mL of Milli-Q water in a 250 mL beaker, and then, solution pH was adjusted to 8.5 with 4 M NaOH; afterward, this solution was transferred to a 100 mL volumetric flask. Subsequently, a total of 50 mL solution was pipetted out and then passed through an ion exchange resin (732-Na) column; after that, this resin column was washed with Milli-Q water (flow rate, 5.5−6.0 mL min⁻¹) until the pH of the effluent was neutral. Finally, the effluent was collected and transferred to a 250 mL volumetric flask and then fixed to the given volume of 250 mL by using Milli-Q water as the test solution. One test solution (100 mL) was adjusted to pH 3 with 0.5 M HNO₃ and then titrated to pH 10 with 0.1 M NaOH using an automatic potentiometric titrator (T-860) (stirred on the ice to prevent APP hydrolysis). There were two abrupt rise points during the titration process. One abrupt rise

point happened at pH 3, and another occurred at pH 10. Finally, the volume of 0.1 M NaOH used was recorded between these two abrupt rise points, and it was represented as V_1. Another test solution (100 mL) was transferred to a 250 mL round bottom flask, and then, it was mixed with 50 mL of Milli-Q water and 10 mL of 6 M HCl, and this solution was heated for 6 h. During this procedure, poly-P was completely transformed into orthophosphate. It must be ensured that all volatile vapors were refluxed in the bottom flask through a condenser tube. After that, the solution pH was adjusted to 3 with 0.2 M HNO₃, and then, the solution was titrated to pH 10 with 0.1 M NaOH. The volume of 0.1 M NaOH used between the two abrupt rise points (at pH 4.5 and 9.5) was referred to as V_2. The polymerization degree of the APP fertilizer was calculated by the formula 4:

$$\text{Average polymerization degree } (n) = \frac{\text{moles of PO}_4^{3-}}{\text{moles of APP}} \tag{4}$$

The polymerization rate (Poly-P/Total-P) referred to the percent of the polyphosphate (Poly-P) accounted for total-P in APP. It was calculated by the formula 5:

$$\text{Polymerization rate (\%)}$$
$$= \frac{(\text{Total-P content})-(\text{Ortho-P content})}{(\text{Total-P content})} \tag{5}$$

Orthophosphate (Ortho-P) of APP was determined according to the method reported by Dick and Tabatabai (1977).[35] It involves a rapid formation of blue-colored molybdenum by the reaction of orthophosphate with molybdate ions in the presence of ascorbic acid, trichloroacetic acid, and citrate−arsenite reagents to prevent further hydrolysis of APP in the acid condition. N content (N %) in APP fertilizers was determined following the Kjeldahl method reported by Tate (1994).[36] Total-P content (P₂O₅%) in APP fertilizers was measured by using the quinolone molybdophosphate gravimetric method, as described by Shaver (2008).[37] Meanwhile, the nitrogen (N) and phosphorus (P) recovery rates were obtained in this study. They were calculated by the formulas 6 and 7:

$$\text{N recovery rate} = \frac{C_n * m_{\text{APP}}}{C_N * M_{\text{Urea}}} \tag{6}$$

$$\text{P recovery rate} = \frac{C_p * m_{\text{APP}}}{C_p * M_{\text{phosphate}}} \tag{7}$$

where C_n and C_N are the N content in urea and APP, respectively; C_p and C_P are the P content in phosphate raw

materials and APP, respectively; m is the weight of APP; and M_{urea} and $M_{phosphate}$ are the weight of urea and phosphate materials, respectively.

The pH value of the APP sample was determined at an APP: water ratio of 1:5 with a pH meter (PHS-2F and DDS-11A, Shanghai INESA Scientific Instrument Co., Ltd).[38] The solubility of APP was measured according to the method reported by Wu et al. (2010)[14] by the dry weight method. The salt index of APP was measured according to the method reported by Latifian et al. (2012).[39] Briefly, an aliquot of 1.0 g of APP fertilizer and sodium nitrate was dissolved with 200 mL of Milli-Q water in a beaker. After 24 h, the electrical conductivity of solution was measured using a conductivity meter (DDS-11A, Shanghai INESA Scientific Instrument Co., Ltd).

The FTIR spectra were recorded using a Nicolet MAGNA-IR 300 spectrophotometer. APP samples were mixed and pressed into tablets with KBr powders. The XRD analysis spectra were recorded with a rotating anode X-ray diffractometer (Japan Rigaku D/Max-Ra, Tokyo, Japan) equipped with Cu Kα (λ = 0.1542 nm) radiation at 2θ values ranging from 10 to 40°.

Statistical Analysis. Data statistical analysis was performed using SPSS 21.0 (Statistical Graphics Corp, Princeton, USA), and treatment effects were analyzed by one-way analysis of variance, followed by Duncan's multiple range tests at a significant difference level of $p < 0.05$. All data were presented as the means ± standard deviation (n = 4, SD). A comprehensive balance method was employed to obtain the optimal reaction combination parameters of the APP manufacturing in the orthogonal experiment (Tables 1 and 2). Figures 1, 2, 3, 4, and 6 were obtained using GraphPad Prism 8.0 (GraphPad Software, San Diego, USA). Figure 5 was plotted by Microsoft Excel 2013 (Microsoft Corporation, Redmond, Washington).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01999.

Description of the detailed determination method of APP properties (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Liu, Y. L.; Li, B.; Xu, M. J.; Wang, L. L. Highly efficient composite flame retardants for improving the flame retardancy, thermal stability, smoke suppression, and mechanical properties of EVA. *Materials* **2020**, *13*, 1251.

(2) Zhang, T.; Tao, Y.; Zhou, F.; Sheng, H.; Qiu, S.; Ma, C.; Hu, Y. Synthesis of a novel hyperbranched phosphorus-containing polyurethane as char forming agent combined with ammonium polyphosphate for reducing fire hazard of polypropylene. *Polym. Degrad. Stabil.* **2019**, *165*, 207−219.

(3) Ma, C. J.; Xiao, Y.; Puig-Bargués, J.; Shukla, M. K.; Tang, X. L.; Hou, P.; Li, Y. K. Using phosphate fertilizer to reduce emitter clogging of drip fertigation process with high salinity water. *J. Environ. Manage.* **2020**, *263*, No. 110366.

(4) Gao, Y. J.; Wang, X. W.; Shah, J. A.; Chu, G. X. Polyphosphate fertilizers increased maize (*Zea mays L.*) P, Fe, Zn, and Mn uptake by decreasing P fixation and mobilizing microelements in calcareous soil. *J. Soils Sediment.* **2020**, *20*, 1−11.

(5) Vasant, G.; Krishnamurthy, V. N.; Sudha, G.; Manik, D.; Kalyani, P.; Borlaug, N. *The fertilizer encyclopedia.* John Wiley & Sons Ltd. 2009, DOI: 10.1002/9780470431771.

(6) McBeath, T. M.; Lombi, E.; McLaughlin, M. J.; Bünemann, E. K. Pyrophosphate and orthophosphate addition to soils: sorption, cation concentrations, and dissolved organic carbon. *Soil Res.* **2007**, *45*, 237−245.

(7) Wang, X. W.; Gao, Y. J.; Hu, B. W.; Chu, G. X. Comparison of the hydrolysis characteristics of three polyphosphates and their effects on soil phosphorus and micronutrient availability. *Soil Use Manage.* **2019**, *34*, 664−674.

(8) Weeks, J. J., Jr.; Hettiarachchi, G. M. Source and formulation matter: New insights into phosphorus fertilizer fate and transport in mildly calcareous soils. *Soil Sci. Soc. Am. J.* **2020**, *84*, 731−746.

(9) Wan, B.; Huang, R. X.; Diaz, J. M.; Tang, Y. Z. Polyphosphate adsorption and hydrolysis on aluminum oxides. *Environ. Sci. Technol.* **2019**, *53*, 9542−9552.

(10) Wang, J.; Chu, G. X. Phosphate fertilizer form and application strategy affect phosphorus mobility and transformation in a drip-irrigated calcareous soil. *J. Plant Nutr. Soil Sci.* **2015**, *178*, 914−922.

(11) Holloway, R. E.; Frischke, B. M.; Frischke, A. J.; Brace, D. M.; McLaughlin, M. J.; Lombi, E. *Field evidence for efficiency of fluid fertilisers.* Australian Fluid Fertiliser Workshop, 2004, 11—22. http://hdl.handle.net/2440/42740 (21—22 September 2004).

(12) McLaughlin, M. J.; Bertrand, I.; Lombi, E.; Holloway, B.; Johnston, C. *New fertiliser formulations for highly calcareous soils of South Australia: Final report to South Australian Grain Industry Trust Fund.* Retrieved from http://trove.nla.gov.au/work/3826851?q&versionId=49400766 (23th, Apr. 2008)

(13) Gooch, J.W. Degree of Polymerization. In: Gooch, J.W. (eds) *Encyclopedic Dictionary of Polymers*. Springer, New York, NY. 2011; 25—32.

(14) Wu, K.; Wang, Z. Z.; Liang, H. J. Microencapsulation of ammonium polyphosphate: Preparation, characterization, and its flame retardance in polypropylene. *Polym. Compos.* **2008**, *29*, 854—860.

(15) McBeath, T. M.; Lombi, E.; McLaughlin, M. J.; Bünemann, E. K. Polyphosphate-fertilizer solution stability with time, temperature, and pH. *J. Plant Nutr. Soil Sci.* **2007**, *170*, 387—391.

(16) Liu, G. S.; Chen, W. Y.; Yu, J. G. A Novel Process to Prepare Ammonium Polyphosphate with Crystalline Form II and its Comparison with Melamine Polyphosphate. *Ind. Eng. Chem. Res.* **2010**, *49*, 12148—12155.

(17) Yang, J. X.; Kong, X. J.; Xu, D. H.; Xie, W. J.; Wang, X. L. Evolution of the polydispersity of ammonium polyphosphate in a reactive extrusion process: polycondensation mechanism and kinetics. *Chem. Eng. J.* **2019**, *359*, 1453—1462.

(18) Walter, H.; Heinz, L.; Heumann Hans, D. R.; Hahn Heinrich, D. R.; Manfred, S. Process for the manufacture of ammonium polyphosphate. Knapsack Aktiengesellschaft Koln Federal Republic of. Patent 4104362, 1978 —08—01

(19) Getsinger, J. G. Production of ammonium polyphosphates from wet process phosphoric acid: U.S. Patent 3382059, 1968 —5—7

(20) Chen, Y. L.; Chen, X. J.; Zhang, C. L.; Tu, P.; Deng, L. S. Conversion of ammonium polyphosphate (APP) in acidic soil and its effect on soil phosphorus. *Appl. Ecol. Environ. Res.* **2020**, *18*, 4405—4415.

(21) Li, C. Z.; Hu, Z. P.; Liu, Y. X.; Yu, N. S. Discussion on influencing factors of polymerization rate of ammonium polyphosphate synthesized by phosphoric acid urea method. *Phosphate Compd. Fertil.* **2019**, *34*, 7—9. (In Chinese with an English abstract)

(22) Zhang, Y.; Li, Y. Research progress of preparation methods of ammonium polyphosphate. *Phosphate Compd. Fertil.* **2014**, *3*, 39—43. (in Chinese with an English abstract)

(23) Watanabe, M.; Watanabe, M.; Narita, N.; Sakurai, M.; Suzuki, H. Preparation of ammonium polyphosphate form II from the system of ammonium orthophosphate-urea. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 115—119.

(24) Liu, G. S.; Liu, X. C.; Yu, J. G. Ammonium polyphosphate with crystalline form V by ammonium dihydrogen phosphate process. *Ind. Eng. Chem. Res.* **2010**, *49*, 5523—5529.

(25) Bai, W. W.; Yan, Y. G.; Zhang, G. X.; Jiang, T. J.; Zhu, H. X.; Li, L. J. Method for preparing high-polymerization-ratio water-soluble ammonium polyphosphate, CN. Patent 105967164A, 2016 —9—28

(26) Shen, C. Y.; Stahlheber, N. E.; Dyroff, D. R. Preparation and characterization of crystalline long-chain ammonium polyphosphates. *J. Am. Chem. Soc.* **1969**, *91*, 62—67.

(27) Hodge, C. A.; Motes, T. W. Production of high-quality liquid fertilizers from wet-process acid via urea phosphate. *Fertil. Res.* **1994**, *39*, 59—69.

(28) Schrodter, H.; Stephan, H. W.; Heymer, G. Process for the production of substantially water-insoluble linear ammonium polyphosphates: U.S. Patent 3978195. 1976 —8—31

(29) Liu, R.; Lal, R. Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. *Sci. Total Environ.* **2015**, *514*, 131—139.

(30) He, Z. J.; Liu, G.; Liu, X.; Yu, J. G. Kinetics study on ammonium polyphosphate polycondensation. *Mater. Rev.* **2009**, *23*, 80—86. (In Chinese with an English abstract)

(31) Sedlmaier, S. J.; Schnick, W. Crystal structure of ammonium catena-polyphosphate IV $[NH_4PO_3]$x. *Z. Anorg. Allg. Chem.* **2008**, *634*, 1501—1505.

(32) McCullough, J. F.; Sheridan, R. C.; Frederick, L. L. Pyrolysis of urea phosphate. *J. Agric. Food Chem.* **1978**, *26*, 670—675.

(33) Wang, W. X.; Zhou, S.; Xin, Z.; Shi, Y. Q.; Zhao, S. C. Polydimethylsiloxane assisted supercritical CO_2 foaming behavior of high melt strength polypropylene grafted with styrene. *Front. Chem. Sci. Eng.* **2016**, *10*, 396—404.

(34) Baluyot, E. S.; Hartford, C. G. Comparison of polyphosphate analysis by ion chromatography and by modified end-group titration. *J. Chromatogr. A.* **1996**, *739*, 217—222.

(35) Dick, W. A.; Tabatabai, M. A. Determination of orthophosphate in aqueous solutions containing labile organic and inorganic phosphorus compounds. *J. Environ. Qual.* **1977**, *6*, 82—85.

(36) Tate, D. F. Determination of nitrogen in fertilizer by combustion: Collaborative study. *J. AOAC Int.* **1994**, *77*, 829—839.

(37) Shaver, L. A. Determination of phosphates by the gravimetric quimociac technique. *J. Chem. Educ.* **2008**, *85*, 1097.

(38) Yang, R.; Yi, D. *Ammonium polyphosphate*. Science press: China, 2015; 43—65.

(39) Latifian, M.; Liu, J.; Mattiasson, B. Struvite-based fertilizer and its physical and chemical properties. *Environ. Technol.* **2012**, *33*, 2691—2697.