Supplementary

1. Overview of the three process alternatives of glyphosate production

There are three commercialized processes for producing glyphosate in China. Fig. 1 is a schematic diagram of the three commercialized processes.

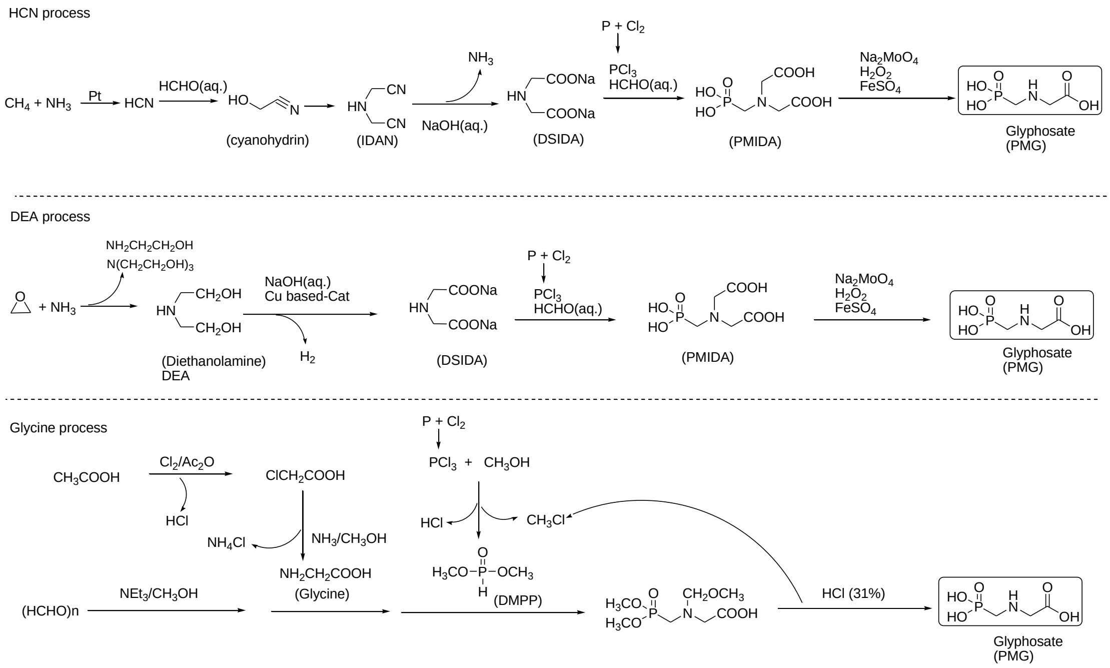

Fig. 1 Schematic diagram of commercialized production processes of glyphosate in China

(1) The HCN process

The HCN process is started with natural gas as one of the raw materials, and HCN and IDAN are key intermediates. At the beginning, HCN is synthesized with natural gas and ammonia, catalyzed by Platinum via the Andrussow process [Note 1]. Then HCN reacts with formaldehyde to get cyanohydrin, followed by cyanohydrin reacts with ammonia to get iminodiacetonitrile (IDAN) [Note 2]. IDAN is hydrolyzed in aqueous sodium hydroxide to get disodium iminodiacetic acid (DSIDA), and ammonia byproduct is recovered and recycled for IDAN preparation. The DSIDA, phosphorous chloride (PCl_3), and formaldehyde are reacted in aqueous solution to get N-phosphonomethyliminodiacetic acid (PMIDA) via the Mannich reaction [Note 3]. At last, PMIDA is oxidized to get the target product glyphosate. The share of this process had been rapidly increased since 2007, and its output capacity took about a

20% share of total glyphosate output in China.

(2) The DEA process

The DEA process is started from ethylene oxide (EO). EO is reacted with liquid ammonia in a continuous tubular reactor to get the mixture of monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). The mixture is rectified to produce three products [Note 4]. The ratio of MEA, DEA, and TEA can be adjusted based on the market demands. DEA is catalytically oxidized to disodium iminodiacetic acid (DSIDA) with a copper-based catalyst under basic condition in aqueous solution [Note 5]. Then DSIDA, PCl_3, and formaldehyde are reacted via the Mannich reaction similar with that of the HCN process to get PMIDA. At last, PMIDA is oxidized to get the target product glyphosate.

The catalytic dehydrogenation of diethanolamine is the key step of DEA process. Monsanto invented the diethanolamine catalytic dehydrogenation technology and awarded a Presidential Green Chemistry Challenge Award. The capacity share of the DEA process in China is nearly 20 percent.

(3) The glycine process

The glycine process is the most widely used process in China, taking a 60% share of the glyphosate output [Note 6]. The glycine process is started with glycine, dimethylphosphonate (DMPP) and paraformaldehyde as key raw materials. At the beginning, paraformaldehyde undergoes depolymerization catalyzed by triethylamine in anhydrous methanol. Successively it reacts with glycine and DMP via the Mannich reaction, then concentrated aqueous hydrochloric acid (31%) is added to the solution obtained above and heated to reflux, thus the target product glyphosate is formed. This process is almost a one-pot process. Glycine is mainly prepared by reaction of chloroacetic acid with ammonia in methanol solution. Chloroacetic acid is synthesized by chlorination of acetic acid with chlorine. DMPP is prepared by reaction of PCl_3 with anhydrous methanol via the Arbuzov reaction. Methylchloride, which is the core byproduct both in DMPP preparation and hydrolysis of the Mannich reaction products, is recovered and reused as a start material for organic silicon products. Glycine can also be prepared with ammonia and cyanohydrin [Note 7].

As for the three manufacturing processes, the glycine process is the pioneer commercialized in China, the DEA process and HCN process are commercialized in a late stage. The Andrussow process for HCN production and the cyanohydrin preparation process have been well-done in China with a long history. In 2005, a great improvement of IDAN manufacturing from cyanohydrin and ammonia made the HCN process a grand step forward in China, and its output increased rapidly.

Oxidation of PMIDA to PMG is another one of the most important cores of the CH4-HCN-IDAN process and DEA process. The evolution footsteps of PMIDA oxidation to PMG is as following: concentrated sulfuric acid oxidation → transition metal catalytic hydrogen peroxide oxidation → noble metal catalytic hydrogen peroxide oxidation → active carbon catalytic hydrogen peroxide oxidation → noble metal loaded active carbon catalytic air or oxygen oxidation [Note 8]. Up to now, the noble metal loaded active carbon catalytic air or oxygen oxidation process is the most effective one with high selectivity, which represents the developing trend of PMIDA oxidation to PMG. A sodium tungstate catalyzed hydrogen peroxide oxidation process is generally applied in China, with a total oxidation yield of 87%. The catalytic air oxidation process is much cleaner than sodium tungstate catalytic oxidation process. Recently, the commercialization of catalytic air oxidation of PMIDA to PMG in China is in a pilot scale with several hundred tonnes a year.

Note 1: Refer to a representative patent of the HCN manufacture process: US2782107.

Note 2: Refer to representative patents of the IDAN manufacture process: US4895971, US4949909, and US5187301.

Note 3: Refer to a few representative patents of the PMIDA manufacturing process: US4724103, US4775498, US5688994, and CN 1329006A.

Note 4: Refer to a few representative patents of the synthesis of MET, DEA, and TEA in a continuous tubular reaction manner with EO and liquid ammonia as starting materials: US4355181, CN 1049653, CN 101560159A, CN 101613289A, and CN 101613290A.

Note 5: Refer to a few representative patents of catalytic dehydration of the DEA process: US5292936, US5367112, US5627125, US5739390, and CN 1398850A.

Note 6: Refer to two representative patents of the glycine process for glyphosate: CN1445231 and CN1939927.

Note 7: Refer to two representative patents of glycine preparation: US3875221 and ZL200310100366.8.

Note 8: Refer to a few representative patents of PMIDA oxidation to PMG process: US3969398,

US395002, US4147719, CN 85102099, EP0472693, US5942643, CN02829008.9, US6586621, and WO2004002622.

2. Mass balance analysis of the three alternatives

Table S1 Mass balance analysis of the HCN process

		Unit	Input								Output	
			CH_4	H_2SO_4	HCHO	NH_3	NaOH(aq.)	P	Cl_2	H_2O_2	PMG	$(NH_4)_2SO_4$
Number of atoms	C	/	1		1						3	
in molecular	H	/	4	2	2	3	1			2	8	8
	O	/		4	1		1			2	5	4
	N	/				1					1	2
	S	/		1								1
	P	/						1			1	
	Cl	/							2			
	Na	/					1					
Molecular weight		/	16	98	30	17	40	31	71	34	169	132
Purity		%	96	98	37	99	30	99	99	30	95	95
Material consumption per PMG output		kg/t	562	314	2189	407	2010	292	1080	810	1000	436
E Factor		kg/kg	4.3									
Carbon element		kg	404		324						202	
Nitrogen element		kg				332					79	88
Phosphorous element		kg						289			174	
Chlorine element		kg							1069			

Table S2 Mass balance analysis of the DEA process

		Unit	Input										Output		
			EO	NH_3	NaOH(30%)	Cu-Cat	P	Cl2	HCHO(30%)	H_2O_2(30%)	Cat	$FeSO_4$	PMG	MEA	TEA
Number of atoms	C		2						1				3	2	6
in molecular	H		4	3	1				2	2			8	7	15
	O		1		1				1	2		4	5	1	3
	N			1									1	1	1
	S											1			
	P						1						1		
	Cl							2							
	Br														
	B														
	K														
	Na				1										
	Fe											1			
Molecular Weight			44	17	40		31	71	30	34		152	169	61	149
Purity			99%	99%	30%	99%	99%	99%	30%	30%	99%	95%	95%	99%	99%
Material consumption per PMG output		kg/t	1781	423	2350	14	292	1080	950	810	5	30	1000	770	475
E factor		kg/kg													
Carbon element		kg	962						114				202	300	227
Nitrogen element		kg		343									78.7	175	44
Phosphorous element		kg					289						174		
Chlorine element		kg						1069							

Table S3 Mass balance analysis of the glycine process

		Unit	Input										Output				
			HAc	Ac_2O	Cl_2	$(CH_2)_6N_4$	NH_3	CH_3OH	PFA	P	Et_3N	NaOH	HCl	PMG	CH_3Cl	$CH_2(OCH_3)_2$	NH_4Cl
Number of	C	/	2	4		6		1	1		6			3	1	3	
atoms	H	/	6	6		12	3	4	2		15	1	1	8	3	8	4
in molecular	O	/	2	3				1	1			1		5		2	
	N	/				4	3				1			1			1
	S	/															
	P	/								1				1			
	Cl	/			2								1		1		1
	Na	/										1					
Molecular weight		/	62	102	71	140	45	32	30	31	101	40	36.5	169	50.5	76	53.5
Purity		%	99	99	99	99	99	99	99	99	99	30	31	95	98	98	98
Material consumption per PMG output		kg/t	514	49	1955	58	292	1796	482	330	40	850	137	1000	1556	500	460
E Factor		kg/kg	5.8														
Carbon element		kg	197	23		30		667	191		28			202	362	232	
Nitrogen element		kg				23	238				5.5			79			118
Phosphorous element		kg								32				174			
Chlorine element		kg			1935								41		1072		299

Table S4 Sensitivity of the weight of economic metrics

Criteria	Metrics	HCN Process	DEA process	Glycine Process	Cost index weighted 20%			Cost index weighted 30%		
					HCN Process	DEA process	Glycine Process	HCN Process	DEA process	Glycine Process
Synthetic complexity	Number of chemistry steps	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
Process material intensity (PMI)	PMI	3	2	1	0.16	0.11	0.05	0.06	0.04	0.02
	Carbon input per glyphosate output	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
	Nitrogen input per glyphosate output	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
	Phosphorous input per glyphosate output	2	2	1	0.11	0.11	0.05	0.04	0.04	0.02
	Chlorine input per glyphosate output	2	2	1	0.11	0.11	0.05	0.04	0.04	0.02
Efficiency of key elements	Carbon efficiency	1	2	3	0.05	0.11	0.16	0.02	0.04	0.06
	Nitrogen efficiency	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
	Phosphorous efficiency	2	2	1	0.11	0.11	0.05	0.04	0.04	0.02
Energy efficiency	Energy consumption per glyphosate output	3	1	2	0.16	0.05	0.11	0.06	0.02	0.04
Nature of waste	Elemental carbon in waste per glyphosate output	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
	Elemental nitrogen in waste per glyphosate output	1	3	2	0.05	0.16	0.11	0.02	0.06	0.04
	Elemental phosphorous in waste per glyphosate output	2	2	1	0.11	0.11	0.05	0.04	0.04	0.02
	Elemental chlorine in waste per glyphosate output	1	1	2	0.05	0.05	0.11	0.02	0.02	0.04
Economic metrics	Cost of raw material for producing 1,000 kg of glyphosate	3	1	2	0.16	0.05	0.11	0.90	0.30	0.60
Toxicity of materials	LD_{50} or LC_{50} of the most toxic material used	1	2	2	0.20	0.40	0.40	0.02	0.04	0.04
Total score		26	35	28	1.53	2.16	1.79	1.36	0.98	1.12

Fig. S1 Price (yuan/tonne) of glyphosate in WYNCA during 2006 to 2012

Note: WYNCA is the top one producer of glyphosate in China with glycine process. Its main page is http://www.wynca.com/en/index.html. Accessed on April 23, 2012.

Source: http://www.askci.com/news/201204/01/0117264554170.shtml, Accessed on April 23, 2012.